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LXXXI. *The Intensity of Reflexion of X-Rays by Crystals.* *By* W. LAWRENCE BRAGG, *F.R.S., Professor of Physics, Manchester University*; C. G. DARWIN, *F.R.S., Professor of Mathematical Physics, Edinburgh University*; *and* R. W. JAMES, *Senior Lecturer in Physics, Manchester University* *.

THE paper is a general review of formulæ that describe the intensity of the reflexion of X-rays from crystals.

Two formulæ have been used, one applicable to perfect crystals, the other to a mosaic of small fragments. The main object is to determine the scattering of radiation by the atom, and it is necessary to know which formula is applicable.

Numerical comparison shows that rock-salt, fluorspar, and barytes approximate closely to the imperfect type, while calcite is intermediate.

Various corrections are discussed which must be applied to crystals of intermediate character.

1. INTRODUCTION.

THE authors were privileged recently to attend a conference, organized by Prof. P. P. Ewald, of the Technische Hochschule of Stuttgart, at which the question of intensity of X-ray reflexion was the chief subject of discussion. The members of the conference were P. P. Ewald,

* Communicated by Prof. W. L. Bragg.

M. v. Laue, L. Brillouin, R. W. G. Wyckoff, H. Mark, I. Waller, A. D. Fokker, P. Debye, K. Herzfeld, H. Ott, and ourselves, and it was held at Holzhausen, on the Ammersee, in Bavaria, in September 1925. We wish to take this opportunity of recording our gratitude to Prof. Ewald for having arranged the conference. It afforded a unique opportunity of exchanging views, and was the greatest inspiration for future work.

The subject of intensity of reflexion has been dealt with by us in several theoretical and experimental papers. The present review of our work, and amplification of certain parts of it, is a direct result of the conference, where the aspects of the subject in which we are particularly interested were very fully discussed. It is impossible to assign credit for some of the ideas which arose in the discussion, and we must rest content with a general acknowledgment to all the other members. One fact which emerged as a result of the discussion was that certain points in our previous papers had suffered in clearness through an attempt to put them concisely, and part of the present paper is devoted to expanding these arguments into a more intelligible form.

Renewed interest in the whole question of intensity of reflexion has been recently excited by the elegant analysis due to Prof. Ewald *. He has treated the problem of reflexion by a perfect crystal, and has placed on a sound mathematical basis the interaction of the X-ray waves and an organised array of atoms. This has raised the question of how far actual crystals conform to this standard, which it is our chief aim to discuss here.

Note.—The following are the chief papers of our own in chronological order to which we shall refer by abbreviated titles. We may also here give the meanings of some of the chief symbols used in them, especially as the notation was not quite uniform :—

Darwin, Phil. Mag. vol. xxvii. p. 315, 1914	D I.
„ „ „ vol. xxvii. p. 675, 1914	D II.
Bragg, James, & Bosanquet, Phil. Mag. vol. xli. p. 309, 1921...	BJB I.
„ „ „ „ „ vol. xlii. p. 1, 1921 ...	BJB II.
„ „ „ „ „ vol. xliv. p. 433, 1922.	BJB III.
Darwin, Phil. Mag. vol. xliii. p. 800, 1922	D III.

The following symbols are common to all :—

Wave-length	λ
Linear absorption coefficient	μ
Number of lattice units per c.c.	N

* Ewald, *Phys. Zeitschr.* vol. xxvi. pp. 29–32 (1925).

The following are divergent :—

	D I, II.	BJB I, II.	D III.	Here.
Angle of reflexion.....	ϕ	θ	θ	θ
Arbitrary angle of setting ...	θ	$\theta+\epsilon$	$\theta+u$	$\theta+u$
Amplitude of wave scattered by an atom at angle 2θ	$f(2\theta, \lambda)$	$\frac{e^2}{mc^2}\mathrm{F}(2\theta, \lambda)$	$f(2\theta, \lambda)$	$\frac{e^2}{mc^2}\mathrm{F}(2\theta, \lambda)$
Integrated reflexion	...	$\mathrm{E}\omega/\mathrm{I}$	ρ	ρ
Distance between successive planes of lattice	a	d	a	a

The advantage of using F instead of f is that it is dimensionally a pure number, and equal to unity for a single electron.

We may also here note certain derived quantities that play an important part in the work.

The amplitude of the wave scattered by a single plane is

$$q = \mathrm{N}\frac{e^2}{mc^2} \cdot \frac{\mathrm{F}\lambda a}{\sin\theta}.$$

The quantity actually measured in imperfect crystals is

$$\mathrm{Q} = \left(\mathrm{N}\frac{e^2}{mc^2}\mathrm{F}\right)^2 \frac{\lambda^3}{\sin 2\theta}.$$

2. Two Formulæ for Intensity of Reflexion.

The question of the intensity of X-ray reflexion is full of difficulties. Any mathematical expression calculated to give the relationship between incident and reflected energy of radiation for a definite experimental disposition contains a number of factors which need to be evaluated. The three factors which are of especial importance depend on

(*a*) The amplitude of the wave scattered by each individual atom of the crystal, for definite directions of incident and scattered beam.

(*b*) The effect of the heat motion of the atoms, giving rise to the temperature factor which reduces the intensity of reflexion as the temperature of the crystal is raised. The existence of this factor* was originally pointed out by Debye, and its effect was first observed by Sir W. H. Bragg.

(*c*) The interaction of the waves scattered by the atoms of the crystal which are in a more or less orderly arrangement.

* *Verh. deutsch. Phys. Ges.* xv. pp. 678, 738, and 867.

In order to make any advance, the last of these factors must be satisfactorily evaluated. If this can be done, there is hope of a direct determination of the second factor by experimental measurements at different temperatures, and so of a determination of the first factor by measuring the intensity of reflexion from a number of types of crystal.

The reward of accurate results is great, since they will yield more direct information as to the positions of the electrons in the atom than is obtainable by any other methods. This must be regarded as the main objective, but a knowledge of the scattering powers of the atoms is also essential to the application of X-rays to discover the structure of complex crystals. After fifteen years of crystal analysis we are not in possession of a means of utilizing to the full the very accurate intensity measurements which can easily be made, and have to be content with qualitative tests. All who have worked in this field will appreciate the unsatisfactory nature of the arguments on which analyses are based.

The difficulty in the mathematical calculation of the last factor arises from the nature of the crystals with which we have to work. On the one hand, an orderly arrangement of atoms is present, since all the X-ray diffraction effects arise from such an arrangement. The accurate comparative measurements of X-ray wave-lengths, extending to five significant figures, show that the atoms in a crystal are arrayed in a very perfect manner. On the other hand, it is clear from experimental results that this perfection has its limits. The orderly arrangement does not extend over the whole volume of the crystal from which the reflected radiation originates, and calculations based on the supposition of an absolutely perfect crystal lead to results which are at variance with experiment. There is no question here of a small correction to be applied on account of the imperfection of the crystal. The observed intensity of reflexion may be from ten to fifty times as great as that given by calculations. This shows the necessity of taking into account the actual nature of the crystal, and the caution with which calculations must be applied.

It will simplify the discussion to consider two extreme cases of crystalline arrangement. Some kind of regular arrangement must, of course, be postulated in order that diffraction effects may be observed. On the one hand, a crystal may be regarded as a *mosaic* composed of small crystalline fragments which are approximately parallel to each other, but whose orientations are distributed through

an angular range of many minutes of arc on either side of a mean direction. All atoms within each fragment are regarded as being in perfect arrangement. The number of atoms in each fragment is so small that their effect on each other when diffracting radiation may be neglected. This is the extreme case of an imperfect crystal, and may be termed the *ideally imperfect crystal*, or *mosaic crystal*. A very simple mathematical expression gives the intensity of the diffracted radiation. Experimental results seem to show that many crystals do in fact approach this ideal type of imperfection. Calculation shows that the homogeneous fragments must not be more than a few thousand atomic planes in depth in order that the mathematical expression may be valid.

On the other hand, we may suppose the crystal to be absolutely perfect. The physical significance of this statement can also be analysed. It means that the small homogeneous fragments of crystal are arranged so regularly that their orientations do not vary by more than a fraction of a second of arc. An entirely different mathematical formula, but one which is again of a very simple type, applies to the diffraction of X-rays by such a crystal. The intensity of reflexion calculated by the second formula is only a fraction of that calculated by the first formula. Experiment has not yet indicated that this ideal perfection is realized in actual crystals. It appears to be the case that all crystals are neither ideally perfect nor ideally imperfect, but have a structure which lies between the two extremes, and in most cases much closer to the ideally imperfect.

As far as we are aware, the expressions for these two cases were first given by one of us in 1914 in the papers D (I) and D (II). In order to give the expression a precise form which may be used for quantitative work the experimental arrangements must be defined. At the date of those papers it was usual to work without slits so that the whole spherical wave fell on the face of a fixed crystal. Some part of this would be at the proper angle, and the sheet of radiation would be effectually limited only by the *length* of the slit of the ionization chamber. This method has proved not so convenient in practice as another due to Sir W. H. Bragg. Here the incident beam is defined by slits, so as to be approximately parallel, and the crystal is rotated with constant angular velocity through the settings for which reflexion occurs. It is obvious that there is a very close relationship between the methods, since in each the crystal is equally exposed to radiation at all angles near the angle of reflexion—in the first

because of the divergency of the incident beam, and in the second because of the uniform rotation of the crystal. In consequence of this it is very simple to translate the formulæ of D (I) and D (II) into the corresponding expressions for the other method, and the latter have the advantage of not containing such quantities as the length of the slit and the distance from source to observing-chamber. In quoting these formulæ we shall express them in the second form without further explanation.

The amount of the reflexion is experimentally described by means of the "Integrated Reflexion," which is measured in the following way. If θ is the angle of reflexion, at near settings of the crystal there will be a certain amount of radiation reflected, and its effect in the observing-chamber will be proportional to the time the crystal is so set. Thus, if we observe that on turning right through the region of reflexion the energy obtained is E, we must expect that the reflexion will be measured by $E\omega$, where ω is the angular velocity of turning. It was in fact observed by Sir W. H. Bragg* that this quantity was constant for different specimens of a crystal although the width of the region of perceptible reflexion varied widely. The quantity $E\omega$ is to be compared with I, the energy produced by the incident beam in the observing-chamber in one second. The ratio $E\omega/I$ or ρ is the integrated reflexion. It is of no physical dimensions, and has the great advantage over the quantities worked out in D (I) and (II) that it is independent of the sizes of slits and all the purely geometrical features of the experiment.

It is in some ways convenient to interpret ρ as follows. Conceive that the radiation was perfectly reflected when it struck the crystal within a given range of angles, and was not reflected at all outside this range. As the crystal rotates with an angular velocity ω, it reflects the incident radiation I for a short time t. The total amount reflected, E, will be equal to It, so that $\frac{E}{I}$ measures the time t, and $\frac{E\omega}{I}$ measures the angular range ωt over which total reflexion takes place. The integrated reflexion ρ is thus the angular breadth of this region (in circular measure). This way of regarding the matter has a very direct application to the case of the perfect crystal.

* W. H. Bragg, Phil. Mag. xxvii. p. 881 (1914).

The formula of D (I), p. 322 (suitably modified), is

$$\rho = \frac{Q}{2\mu} = \left(N \frac{e^2}{mc^2} F\right)^2 \lambda^3/2\mu \sin 2\theta.$$

The temperature factor $e^{-B(T)\sin^2\theta}$ and polarization factor $\frac{1+\cos^2 2\theta}{2}$ are omitted, and a lattice of only one type of atom is here being used.

The formula (1) was originally worked out on the assumptions which Laue made when he first calculated the diffraction of a crystal; that is to say, the crystal was assumed perfect, but all interactions between the waves scattered by the atoms were neglected. The work, however, itself showed that these assumptions were inadequate (the argument is outlined in § 8 below), and it was conjectured in D (II) that it was actually the correct formula to apply to an ideally imperfect crystal. This was proved in BJB I. However, it is shown in D (I), p. 331, that this formula gives a reasonable value for the ratio between incident and reflected radiation for rock-salt. Moseley and Darwin* measured this ratio under definite experimental conditions, using white radiation. The value obtained agrees with the formula if the average effective number of electrons in sodium and chlorine is about ten, which is of the right order. The applicability of the formula has been confirmed by Compton † and Bragg, James and Bosanquet using monochromatic radiation and a rock-salt crystal (BJB I, II). We have extended the investigation to several other crystals as described below.

Formula (1) applies to the case of the ideally imperfect crystal. In order that a crystal may be considered to be of this type, its homogeneous fragments must be less than a certain size. They must be so small that the effect on any atom of the waves scattered by others in the fragment is negligible. Even when this is the case, an effect we have called "secondary extinction" modifies the formula; but this effect is amenable to experimental measurement, and will be dealt with later in this paper.

In D (II) a formula is deduced for the reflexion from a crystal which is absolutely perfect. At any depth in the crystal there exists a wave proceeding in the direction of the incident wave ‡, and a reflected wave. As each crystal

* Phil. Mag. xxvi. p. 210 (1913).

† A. H. Compton, Phys. Rev. ix. p. 1 (1917).

‡ The direction is really slightly modified by the refractive index of the crystal.

plane is crossed, the incident wave is partly reflected and modifies the amplitude of the main reflected wave, and this latter is partly reflected and modifies the incident wave. A set of difference equations is solved to obtain the final result. The amplitude of reflexion is shown to rise as the mean angle of reflexion θ is approached. When the glancing angle is equal to $\theta - s$, s being a small angle of the order of a second, reflexion becomes perfect and remains perfect till it is equal to $\theta + s$. After that point it rapidly diminishes. In this

$$s = q\lambda/2\pi a \cos\theta = \mathrm{N}\frac{e^2}{mc^2}\mathrm{F}\lambda^2/\pi \sin 2\theta \quad . \quad . \quad (2)$$

The expressions for the amplitude of reflexion in the three regions are given on p. 680, D (II).

Considering only the region of total reflexion, we get at once an expression for the integrated reflexion from a perfect crystal, for we have seen above that it is numerically equal to the angle $2s$. It is shown on p. 682, D (II), that this region contributes $\frac{3}{4}$ of the integrated reflexion, and that the regions on either side contribute the remainder. From this it follows that the total integrated reflexion is given by

$$\rho = \frac{8s}{3},$$

and substituting for s,

$$\rho = \frac{8}{3\pi}\mathrm{N}\frac{e^2}{mc^2}\mathrm{F}(2\theta, \lambda)\lambda^2\frac{1}{\sin 2\theta}. \quad . \quad . \quad (3)$$

This expression must be multiplied by a temperature factor $e^{-\frac{1}{2}\mathrm{B(T)}\sin^2\theta}$ and polarization factor $\frac{1 + |\cos 2\theta|}{2}$. Contrasting (1) and (3), it will be seen that certain factors in (3) are raised to the second power in (1).

3. Proportionality of Intensity with Structure-Amplitude or with Square of Structure-Amplitude.

One of the most striking differences between these two formulæ is the following. In (3) the integrated reflexion is proportional to the amplitude reflected by a single plane of atoms in the crystal, in (1) it is proportional to the square of the amplitude. It is customary to make the latter assumption. Should we not rather expect it to be proportional to the structure amplitude itself?

In the recent paper referred to above, Ewald has raised

this question. He has obtained formulæ for the reflexion from a perfect crystal which agree with that given is D (II). They are, however, based on a more rigorous mathematical investigation carried out in a very elegant manner. He arrives at the result that about 80 per cent. of the integrated reflexion occurs in the region of total reflexion, as compared with the 75 per cent. calculated in D (II). Otherwise the formulæ are identical. At the recent conference, formula (3) was confirmed by I. Waller, who had independently evaluated the integral and arrived at the same factor of 75 per cent.

Ewald quotes cases where measurements of integrated reflexions indicate that they are proportional to structure amplitude rather than to the square of this quantity. He concludes: "Im Gegensatz zu der üblichen Auffassung ergibt sich die Intensität, so weit sie von der Totalreflexion herrührt, proportional zum Betrag der Strukturamplitude selbst nicht zu deren Quadrat."

Ewald points out the manner in which the structure amplitude influences the intensity of reflexion. Whatever the value of the structure-amplitude, reflexion is perfect over a finite range of angle. The breadth of the range, however, is proportional to the structure-amplitude, and so the effect of crystal structure on the relative intensity of spectra arises. This result follows directly from formula (2) above where s is proportional to q, the fraction of radiation reflected at a single crystal plane. The formula for the ideally imperfect crystal makes the intensity of reflexion to be proportional to q^2. It is our object in this paper to discuss which type of formula should be applied to actual crystals*.

Many facts show that crystals must be regarded as imperfect in the sense discussed here. (*a*) It was first shown by Darwin that the strength of reflexion by a crystal of rock-salt was far greater than could be accounted for by the formula (3). According to this formula, total reflexion in the first order should be included in a region $6''$ in breadth

* The most striking case of this nature is that of the diamond crystal, investigated by W. H. Bragg (Proc. Phys. Soc. Lond. vol. xxxiii. p. 304, 1921). A small diamond crystal was bathed in X-rays, and rotated through each position of reflexion. The planes give structure amplitudes of two types, one being $\sqrt{2}$ times as great as the other for corresponding angles of incidence. The ordinates of the two curves, which pass through points representing *intensities* of reflexion for planes of each type, are also in the ratio $\sqrt{2}$ to 1. If intensity were proportional to the square of amplitude they should be in the ratio 2 : 1.

(p. 680, D (II)) for a wave-length of 1·11 Å. A total reflexion over this range only accounts for one-tenth of the efficiency of reflexion of white radiation observed by Moseley and Darwin (D (II), p. 684). It was concluded in D (II) for this reason that crystals must be imperfect, and it was shown that the formula for the ideally imperfect crystal gives a much more satisfactory estimate of the efficiency of reflexion. (*b*) The formula for reflexion by a perfect crystal does not contain the absorption coefficient of X-rays in the material. Experiment shows that the absorption coefficient plays a large part in influencing the efficiency*. (*c*) A direct experimental test shows that most crystals reflect monochromatic X-rays over so wide a range of angles that they must be composed of a mosaic of fragments only approximately parallel. In certain cases, however, the imperfection is too small to be observed in this way (calcite, diamond)†. In the case of calcite, as we shall see, other tests reveal the fact that it is not a perfect crystal for which the reflexion is given by formula (3).

4. Primary and Secondary Extinction.

It appears to us that the most promising method of discovering the physical nature of the crystal, and of deciding what formulæ to use, consists in careful measurements of the integrated reflexion. We may expect to find these measurements to lie between two extremes—a lower limit given by the formula for the perfect crystal, and an upper limit given by the formula for the ideally imperfect crystal. In order to estimate the degree of perfection we must have some idea of the behaviour of intermediate types, and this has been worked out in D (III). In this paper the ideally imperfect crystal is regarded as the standard, and the integrated reflexion is supposed to be lowered below this standard by two phenomena which are called primary and secondary extinction, which we may now explain. The formula for the perfect crystal shows that total reflexion takes place over a range of several seconds of arc in the case of the more powerful reflexions given by simple planes. In such a

* W. H. Bragg, Proc. Roy. Soc. A, vol. lxxxix. p. 430 (1914).

† A very interesting note on imperfection of crystals has been published by H. Mark while this paper was being prepared (*Naturwissenschaften* 13, 49/50, p. 1042, Dec. 1925). By examining the divergence of the reflected X-ray beam from a diamond crystal at a distance of ten metres from the crystal, he has shown that some crystals of diamond are very nearly perfect.

crystal all the reflexion must take place in a layer very close to the surface, for the inner parts of the crystal receive no radiation at the correct angle for reflexion, since this radiation has been diverted by the upper layers. If, however, the crystal departs from ideal perfection, and the lower layers are inclined at an angle of more than a few seconds to the upper layer, they will be able to reflect radiation which has traversed the upper layers. *Any departure from perfection increases the integrated reflexion to a value greater than that given by formula* (3).

We have called this shielding of lower layers by parallel upper layers of the *same homogeneous fragment* of crystal "*primary extinction.*" It is at its maximum in the perfect crystal, and in fact it is not necessary to use the conception when dealing with the perfect crystal since formula (3) can be applied at once. It is convenient to use it when dealing with crystals which are imperfect, but in which the homogeneous blocks are so large that their lower layers are appreciably screened by the upper layers.

The upper limit to the integrated reflexion is given by formula (1) for the ideally imperfect crystal. In this case the homogeneous blocks are so small that every part of them receives its due of radiation. As long as the blocks are sufficiently small for this to be the case, their size and relative orientation do not affect the value of the integrated reflexion. This is only characteristic of the crystal, of the indices of the plane, and of the wave-length, when allowance is made for the effect described in the next paragraph.

A factor comes in which diminishes the integrated reflexion from that given by formula (1) even when the homogeneous blocks are very small. When the primary beam of X-rays traverses the crystal in a direction which permits of reflexion by some of the blocks, its energy is lessened by being partly reflected as well as by being absorbed in the usual way through conversion into β rays*. The existence

* The absorption coefficient of an amorphous substance contains a term arising from the scattering, which is quite small for moderately soft rays. If not insignificant, this term requires special treatment, as the scattering is responsible for the reflected wave. If the atoms had no heat motions, it would be proper to miss this part of μ out, as its effect is allowed for in the secondary extinction below. At actual temperatures there is some general incoherent scattering, and this should be counted in with the true absorption; but the whole matter is involved in the question of the temperature effect, and requires much more thorough treatment. See Waller, "Theoretische Studies zur Interferenz und Dispersionstheorie der Rontgentstrahlen," Uppsala Universitets Årsskrift, 1925.

of this apparent increase in absorption at the reflecting angle was first demonstrated experimentally by W. H. Bragg *. We have called this increase *secondary extinction*. In the case of a given crystal, its value will depend on the law according to which the fragments of homogeneous crystal are orientated, and on the direction in which the rays pass through the crystal. We have shown (BJB II) that in the case of the (200) reflexion from rock-salt the secondary extinction may attain a value half as great as the ordinary absorption coefficient, and very probably in other crystals it attains a much higher value.

Both primary and secondary extinction thus depend on the shielding of lower layers by parallel upper layers which divert X-ray energy which would otherwise be reflected. They may be distinguished as follows. In the case of primary extinction the upper and lower layers form part of the same homogeneous fragment of crystal, so that a phase-relationship exists between waves reflected by them. In the case of secondary extinction the layers are separated by other fragments with a different orientation, so that no such phase-relationship exists. In the first case the calculation deals with amplitude, in the second with intensity.

Both types of extinction tend to diminish the integrated reflexion to a value less than that given by formula (1), which therefore gives an upper limit to the intensity of reflexion.

In comparing the observed values of integrated reflexions with those given by formulæ (1) and (3), we are confronted by the difficulty of estimating the factor denoted by $F(2\theta, \lambda)$ and the temperature factor. The chief object of our experiments on intensity must be to evaluate F, and thereby the arrangement of the electrons in the atom ; but, for our present purpose, as we are only working out the order of the effect to be expected by using the two formulæ for reflexion, we will assume values of F which are known from other evidence to be approximately correct. When θ is small, $F(2\theta, \lambda)$ is equal to A, where A is the number of electrons in the atoms †, which are supposed to be identical

* W. H. Bragg, Phil. Mag. vol. xxvii. p. 881 (1914).

† This assumes that the X-ray frequency is higher than any natural frequency in the atom. For heavy atoms it will be necessary to make an allowance for approximate equality of frequencies. Such a correction can be calculated by the ordinary principles of the theory of optical dispersion. Mark and Szilard (*Zeit. f. Phys.* xxxiii. p. 688, 1925) have obtained direct evidence of an abrupt change in the scattering power of an atom when the frequency of the incident radiation passes through the value characteristic of the absorption edge of the atom.

and arranged in a simple space-lattice (the extension to more complex cases involving several kinds of atoms is obvious). As θ increases, $F(2\theta, \lambda)$ falls away from this value in a way determined by the atomic structure. The values for F must be estimated by postulating probable atomic structures, and so are uncertain *. They are probably not far from the truth, however, for low values of θ, since the limiting value for $\theta = 0$ is definite.

In connexion with the theoretical value for F, the question arises whether an allowance should be made on account of the Compton effect, the change in frequency of part of the scattered radiation. It is conceivable that the change in frequency will prevent interference ; and since part of the scattered radiation is thus changed, an estimate of the scattering power of the atom based on the classical theory and the laws of interference will be too large. This point needs, however, very careful theoretical investigation. From another point of view, if we make use of the close analogy between the Compton scattering and the Doppler effect, the Correspondence Principle suggests that the effect might have little influence in reducing the reflexion.

However this may be, it is evident that the doubt attaching to F applies mainly to large values of θ, since the limiting value for $\theta = 0$ is definite. In the region of small glancing angles ($\sin\theta < 0{\cdot}1$ for Rh Kα rays, for example) the value of F has not fallen greatly from its maximum, and is almost independent of the exact assumptions made as to electronic configuration. In the same region the temperature factor is nearly unity. Extinction plays its most important part for the strong reflexions at small angles, since it is greatest when the integrated reflexion is greatest. *We may therefore hope to estimate the effect of extinction, and get some information about the mosaic structure of the crystal, by comparing calculated and observed intensities of reflexion at small angles where the uncertainty about the other factors at least.*

* Hartree (Phil. Mag. vol. l. p. 289, 1925) has calculated tables from which F curves for all atoms can be deduced. The classical law of scattering by an electron is assumed. The atomic fields for some atoms have been found approximately by numerical analysis of the optical and X-ray spectra, and thus the dimensions of each electronic orbit have been calculated, together with the timespent in every part of it. It is possible to generalize the results and put them in such a form that an approximate F curve for any atom can be constructed very simply. The modified distribution of quantum numbers due to Stoner is assumed, but the difference between F curves calculated with Stoner's or with Bohr's assumptions is quite small.

6. Comparison of the Estimates of Intensity given by the Formulæ with Observed Determinations.

(a) *Rock-salt.*—We give in the first place the figures for this crystal because we have investigated it more fully than others. Sufficient experiments have been carried out to enable an estimate of the temperature factor and of the effect of secondary extinction to be made. The effect of temperature on intensity has been measured by one of the authors * between 300° and 800° absolute, and the measurements have recently extended to 100° absolute. Though the experiments at low temperatures are not yet completed, we may estimate the temperature factor at room temperature to be

$$e^{-6\cdot44\sin^2\theta},$$

this being the reciprocal of the factor required to reduce measurements of intensity to absolute zero. In calculating this factor it is safe to assume that formula (1) is true for rock-salt in the higher orders of reflexion, since the effect of both kinds of extinction proves to be very small for weak reflexions. The extinction factors measured by us (BJB II) are, of course, characteristic of the specimens of rock-salt we used, and will not apply to other cases. As has been shown in D (III), the method we employed for determining them gives correct results for secondary extinction, but does not determine primary extinction.

The results of the comparison will be seen from Table I. The first column gives the sine of the glancing angle, the second gives F †. The third and fourth columns give the integrated reflexion calculated by formulæ (3) (perfect crystal) and (1) (ideally imperfect crystal). Columns 5 and 6 show the effect of applying the correction for extinction, and for the temperature factor, the fourth column. In column 7 both corrections have been applied. Column 8 gives the experimental results.

The very great difference between the results of the two formulæ in columns 3 and 4 at low angles will be noticed, the one being one-fiftieth of the other. Extinction makes a large difference to the strong reflexions, but its effect is inappreciable for the high orders. On the other hand, the temperature factor which is nearly unity at low angles has a marked importance in the high orders, reducing reflexions to one-tenth their intensity when $\sin\theta = 0\cdot6$. The figures

* R. W. James, Phil. Mag. vol. xlix. p. 585 (1925).

† The F referred to is $F_{Cl}+F_{Na}$, and the reflexions are all from planes where the contributions from these atoms are in phase.

in the last two columns give a comparison between observed values and those to be expected from an ideally imperfect crystal. They prove that rock-salt must realize closely the true mosaic type.

Rock-salt, NaCl. Rh K_α rays, $\lambda = 0{\cdot}614$ Å. $\mu = 10{\cdot}7$.

Sin θ.	F ($F_0=28$).	$\rho\times10^6$, calculated for perfect crystal.	$\rho\times10^6$, calculated for ideally imperfect crystal.				$\rho\times10^6$, observed.
			No corrections applied.	Corrected for extinction.	Corrected for temperature.	Both corrections applied.	
0·05	26·7	53·98	3004				
0·1	23·2	23·40	1148	725	1076	678	605
0·2	16·7	8·29	284·5	251	220·3	194·5	138
0·3	14·2	4·57	127·5	123·5	71·4	69·2	37
0·4	11·2	2·60	55·5	55·0	19·2	19·1	8·7
0·5	8·3	1·45	21·5	21·5	4·28	4·28	1·5
0·6	6·4	0·86	10·0	10·0	0·98	0·98	

The observed figures are all lower than the calculated figures. If the difference were due to primary extinction arising from high perfection of the crystal, one would expect the difference to be most marked at low angles. The reverse is the case, and it is more reasonable to suppose that the discrepancies are due to errors in the calculation of F. We have used the values given in Hartree's paper *, calculated from his models of the electronic orbits in atoms. There is a general indication in all our results that Hartree's values do not fall away sufficiently fast as θ is increased.

In a strict comparison we should allow for the temperature factor in giving the figures for a perfect crystal, and also calculate the effect of ordinary absorption. This is inappreciable for strong reflexions, but even in a perfect crystal it has an effect for the very weak reflexions. The figures at the bottom of column 3 will be considerably reduced by these corrections. When the amount of energy lost by absorption at a single crystal plane becomes appreciable as compared with that reflected, the formula becomes very complicated. Since the criterion for perfection becomes the more exacting the weaker the reflexion, and we have

* *Loc. cit.*

already good evidence for imperfection in the strong reflexions, it seems unnecessary to evaluate the correct figures at the bottom of the third column. As indicated in D (II), the formula involves elliptic integrals.

(b) *Fluorspar*, CaF_2.—Reflexions for which the calcium and fluorine atoms are in phase have been measured for values of $\sin\theta$ between 0·2 and 0·77. In this case the secondary extinction and temperature factor have not been measured, and the corresponding corrections to the figures calculated for the imperfect crystal cannot be made.

Fluorspar, CaF_2. MoK_α rays, $\lambda = 0{\cdot}710$ Å. $\mu = 31{\cdot}3$.

Sin θ.	F ($F_0 = 38$).	$\rho \times 10^6$, calculated. Perfect crystal.	$\rho \times 10^6$, calculated. Ideally imperfect crystal.	$\rho \times 10^6$, observed.
0·05	36·3	107·8	3622	
0·1	32·4	48·0	1303	
0·2	21·6	15·7	304	112
0·3	14·0	6·6	79·0	47·0
0·4	11·2	3·8	39·6	18·2
0·5	9·9	2·55	19·5	9·0
0·6	8·1	1·60	10·2	4·8
0·7	6·0	0·91	5·0	2·6

The F values for calcium are taken from Hartree's tables. The F curve for fluorine taken from Hartree's tables has been modified, because in this crystal a comparison of the curves for $Ca + F_2$, Ca, and $Ca - F_2$ enables one to deduce that the F values for fluorine fall away more rapidly. F becomes less than 0·5 when $\sin\theta > 0{\cdot}55$. We have similarly modified his values for oxygen in the following comparisons.

The temperature factor and extinction factor will reduce the figures in column 4 so that it again appears that fluorspar is of the imperfect mosaic, rather than of the perfect crystal, type.

(c) *Barytes* $BaSO_4$.—The structure of barytes, analysed by James and Wood*, is more complex than that of the two crystals previously considered, and it is no longer possible to make measurements of reflexions for which all the atoms of the lattice unit are in phase. Since the barium, sulphur, and two of the oxygen atoms lie on symmetry planes

* James & Wood, Proc. Roy. Soc. A, vol. cix. p. 588 (1925).

of reflexion in the crystal, and the only atoms not on these planes are the remaining two oxygen atoms of the molecule, which are very light in comparison, reflexions from these planes are nearly as strong as they would be if all the atoms had been in phase. The strength of these reflexions shows that the crystal approaches the ideally imperfect type. It is therefore justifiable to assume that ρ varies as the square of the structure amplitude, and to use this relation to construct a *normal curve* of intensity of reflexion from the observed results. The points on the normal curve are estimates of what the intensity would be if all the atoms had co-operated. The figures for this normal curve are given in the last column as "observed." In many cases the correction to be applied to the intensities for structure factor is not large, so that the normal curve so constructed cannot be far from the truth.

The absorption coefficient μ for barytes has not been directly measured. The figure 116 for Mo K_α radiation is calculated from tables given by Windgardh *. In the case of other crystals we have found good agreement between the values given by his tables and measurements made with sections of crystal. We have not as yet investigated the extinction factor and temperature factor. The absorption coefficient is so high that the figures for reflexion from a perfect crystal, in calculating which no account of absorption has been made, are meaningless at the higher angles.

Barytes, like fluorspar and rock-salt, appears to be a crystal approaching the ideal mosaic type.

Barytes, $BaSO_4$. Mo K_α rays, $\lambda = 0{\cdot}710$ Å. $\mu = 116$.

Sin θ.	F ($F_0 = 104$).	$\rho \times 10^6$, calculated. Perfect crystal.	$\rho \times 10^6$, calculated. Ideally imperfect crystal.	$\rho \times 10^6$, observed.
0·05	100	140·1	1611	
0·1	89·3	62·4	648·5	462
0·2	65·6	22·5	168	127
0·3	50·5	11·3	61·6	33·8
0·4	41·0	6·59	27·8	11·3
0·5	32·1	3·90	12·3	4·6
0·6	27·0	2·52	6·78	2·06
0·7	24·5	1·55	5·0	

* *Zeitsch. f. Phys.* vol. viii. p. 363 (1922).

(d) *Calcite*, $CaCO_3$.—This case is interesting because calcite appears to approach more closely the perfect crystal. The intensities in the last column are taken from relative measurements by W. H. Bragg *, supported by an absolute determination of a few reflexions †. W. H. Bragg notes the fact that intensity in calcite appears to be proportional to structure amplitude rather than to its square. Ewald comments on this in his paper referred to above ‡.

Calcite. $CaCO_3$. Rh K_α, $\lambda = 0{\cdot}614$ Å. $\mu = 15{\cdot}6$.

Sin θ.	F ($F_0 = 50$).	$\rho \times 10^6$, calculated. Perfect crystal.	$\rho \times 10^6$, calculated. Ideally imperfect crystal.	$\rho \times 10^6$, observed.
0·1	41·2	30·9	1220	240§
0·2	25·6	9·4	280	70
0·3	15·9	3·8	63	27
0·4	12·2	2·08	23·5	8·6
0·5	10·4	1·69	12·5	2·4

The low values of the observed intensities indicate that primary and secondary extinction must be much more important than absorption in reducing the intensity of reflexion. This is in accord with the observed proportionality of intensity to structure amplitude. This very interesting feature indicates the desirability of a more searching investigation.

A crystal which has a high primary extinction for strong reflexions may at the same time behave as a mosaic crystal for weak reflexions. In the latter case the range of perfect reflexion is smaller, and a larger homogeneous block is required in order to give complete reflexion. If the strong

* Phil. Trans. Roy. Soc. A, vol. ccxv. (1915).

† W. L. Bragg, Proc. Roy. Soc. A, vol. cv. p. 16 (1924).

‡ The first measurements of absolute intensity of reflexion by Calcite were made by Compton (Phys. Rev. x. p. 95, 1917), who found that the intensity had a very much smaller value than the mosaic theory would lead us to expect. Davis and Stempel (Phys. Rev. xvii. p. 608, 1921) found that over a small range of angles a calcite crystal acts as a very good reflector of X-rays, as much as 44 per cent. of the radiation being reflected in certain cases. This range of reflexion was confined to about eighteen seconds of arc for the radiation which they used.

§ This figure is an estimate based on the observed intensity 149 for the (200) reflexion.

reflexions show an agreement in order of magnitude between observation and calculation by the mosaic formula (1), one can be certain that the weak reflexions obey formula (1) rigidly. The intensities of these reflexions will give reliable information about the form of the F curves at higher angles, provided that the effect of temperature can be allowed for. A knowledge of the temperature coefficient for NaCl, CaF_2, $BaSO_4$, and other crystals will thus make possible the determination of a set of empirical F curves which should be very useful in crystal analysis.

7. The Estimation of the Degree of Imperfection.

The preceding examples show distinct evidence that some crystals are nearly if not quite ideally imperfect, while in others there is a partial approach to perfection. It thus becomes important to gauge the degree of perfection, and the numerical results suggest that it is natural to regard the ideally imperfect as the standard and to gauge the departure from this. The chief object is to find the form of F ; but in the course of the work we may hope to derive information as to the actual degree of imperfection of any crystal.

The main difficulty in finding F (or, rather, the associated function Q) lies in the evaluation and elimination of the extinction, a process which has only so far been carried out in the case of NaCl. We have pointed out above that there are two types of extinction simultaneously operative and that no process can eliminate one, the primary. The reason for this is that the primary extinction depends on the individual fragments, of which each reflects the rays over a few seconds of arc. If it were possible to obtain readings with the crystal at successive settings at intervals only a fraction of a second apart (the rays must be parallel with this degree of accuracy also), we might fit the results to a formula, find the number of layers in the fragments, and extrapolate to the case of small thickness. But the difficulty of doing this is very great, and we have to be content with the integrated reflexion of the fragments. The result of this is that we do not determine Q, but a lesser quantity Q′. It is shown in D (III), p. 816, that

$$Q' = Q\ (\tanh mq/mq), \quad . \quad . \quad . \quad . \quad (4)$$

where q is the amplitude of the wave reflected from a single plane, and m is the number of planes *.

* We owe to a letter from I. Waller the information that this formula only holds for reflexion at a face. For reflexion through a plate it is somewhat modified.

The matter is quite otherwise for the secondary extinction. This depends on the impoverishment of the radiation striking the deeper fragments on account of the reflexion from the outer ones. In this case it is possible to measure not merely the integrated reflexion, but the actual amount E_u at each setting u of the crystal (compare the curve in BJB II, p. 13). It was suggested in D III that from this curve it should be possible to deduce a function of the setting angle u, called $G(u)$ (pp. 811 and 921), from which Q' could be determined by integration over all values of u. The quantity $G(u)du/Q'$ is the fraction of the crystal by volume in which the fragments are orientated with settings between u and $u+du$. Again, knowing the form of $G(u)$, it should be possible to calculate the extinction coefficient ϵ, this being the addition to be made to the ordinary absorption coefficient in (1) so as to be able to derive Q from the integrated reflexion.

This quantity was directly measured in BJB II by taking the integrated reflexions *through* a set of crystals of varying thickness, instead of making the observations on a single crystal face. When a crystal plate of thickness t_0 is rotated, and the rays are reflected at planes which are at right angles to the plate, the integrated reflexion is given by

$$\rho = Qte^{-\mu t},$$

where $t = t_0 \sec\theta$, and $\mu = \mu_0 + \epsilon$. By plotting ρ against t both Q and μ can be measured. The ordinary coefficient of absorption μ_0 (10·7 for Rh K_α) is measured by passing the rays through the plate at an angle where reflexion does not occur, and so ϵ can be obtained. A value of 5·6 for ϵ when the (200) reflexion is taking place, and of 2·9 for (220), was observed, these values being average ones for the specimens of rock-salt employed.

A calculation in D III made with the object of comparing these values of ϵ with values based on the $G(u)$ curve gave distinctly unsatisfactory results—the calculated value of ϵ was about 1 as compared with the observed of about 5, though the data were perhaps not good enough to condemn the process out of hand. The matter has since been investigated with great skill and accuracy by Wasastjerna*, who obtained much the same results, and there was thus a rather serious discrepancy to be faced. It would appear that this

* By an ingenious slit-system, Wasastjerna explored the amount of radiation reflected at different depths of a crystal face. His value for ϵ is close to that given in BJB II.

discrepancy is due to a fact overlooked in D III. The assumption was made that the crystal was uniform in character throughout, so that all points of its face possess the same $G(u)$. But if the gross structure of the crystal is warped, it is possible that the part illuminated through the top of the slit will reflect best in a different position from that illuminated through the bottom. All parts of the crystal may contribute to measurements of the stationary reflexion E_u, and so the reflexion curve may be spread out quite wide ; but yet the crystal fragments in each part of the face may be strongly concentrated in one direction, with consequent large extinction. In fact $G(u)$ must be regarded as a function of y, the coordinate along the axis of rotation, and E_u as a rather complicated average effect from which the corresponding average for $G(u)$ cannot be derived. The function $G(u)$ which comes into our formula depends on the divergence in orientation from a mean direction of the fragments encountered along the path of a reflected beam, which will be only a fraction of a millimetre in length within the crystal. It depends on the local imperfection, not the gross imperfection, of the crystal.

We may observe that this difficulty does not arise in the experimental method of BJB II, for there only averaged quantities occur throughout ; but it is necessary to assume that the warping was about the same in extent for all plates used.

The other problem is to measure the mean of the depth of the coherent fragments. If Q is known from other sources, we can deduce this by measuring Q′ and so solving (4) for mq, for q is determined by Q. But if the problem is to determine Q, this method is not available. All we can do is to take various crystals of the same substance (of which some should preferably show external signs of being fragmented), and evaluate Q′ for each of them. The greatest value may be presumed to be not far from Q.

The experimental data are insufficient to apply this method yet, but to illustrate it we shall suppose that in the rock-salt above the difference between the last two columns is due to primary extinction.

Then we have $\dfrac{\tanh mq}{mq} = \dfrac{605}{678}$, $mq = 0{\cdot}61$, and since $q = 2 \times 10^{-4}$, we have $m = 3050$ as the average number of planes in a fragment. As pointed out above, it is probable that the difference between 605 and 678 is due rather to an error in F than to extinction. If so, the fragments must be thinner than this.

To summarise :—We have three different types of imperfection—those responsible for primary and for secondary extinction, and the general warping of the crystal. Unless we know F from other sources, the first can only be evaluated by investigating so many crystals that in some the correction is absent. When known it tells us how thick the perfect fragments of each crystal specimen are. The second can be found by direct experiment, and tells us the angular width over which the fragments are spread in each part of the crystal. The third is of the type usually to be seen directly by the surface reflexion of ordinary light. It could be studied by taking reflexion curves with varying lengths of the slits defining the beam of X-rays.

8. The Earlier Arguments in favour of Crystal Imperfection.

The evidence for considering crystals as imperfect is quite conclusive, as shown in § 6 above ; but this conclusion was, in fact, reached in 1914 in D (I) and D (II). The argument as there given is not very clearly expressed, and is enormously complicated by the fact that no double reflexions had then been made, so that the only experimental measure of efficiency of reflexion had to do with white radiation. There were two stages in the argument. In D (I) it was shown that it was not possible to disregard the interactions between the atoms, and in D (II) that, allowing for the interactions as they would occur in a perfect crystal, the total amount reflected was far below the amount observed.

The first argument was as follows :—Supposing that the wave scattered by each atom is too small to influence the others, we can calculate the diffraction pattern of the reflected wave when a fixed crystal is illuminated by the spherical waves from a point-source. The pattern is like those in the lateral spectra of a grating, and the only limitation to the number of lines of the grating is the absorption coefficient of the crystal. A simple calculation shows that the number is enormous, and that the angular breadth of the image is only about 1/100 of a second of arc. We may notice that this in itself is sufficient for the purpose in view, for even if the reflexion in that breadth were perfect, it would make the integrated reflexion equal to about 1/2,000,000, and we now know it to be often more than 1/10,000. In D (I), however, a more cautious line of argument was taken, and one approximating more closely to the experiments. In the first place we assume the formulæ to be correct, and

apply them to the curves of white radiation as measured by Moseley and Darwin. The higher orders of spectra and the peaks of characteristic radiation are easily eliminated, and the result is a curve for E_λ, the distribution of energy in the spectrum (a table of the values is given in D (I), p. 331). Next consider the experimental measure of efficiency of reflexion. The incident waves were limited by a slit, so that their angular aperture was, say, $\delta\theta$ broad. Thus a certain range of wave-lengths would be reflected, say $\delta\lambda$, which would be determined by the relation $\lambda = 2a \sin\theta$, so that $\delta\lambda = \lambda \cot\theta\delta\theta$. The radiation reflected would be proportional to $\delta\lambda$, and the incident radiation through the same slit to $\delta\theta$, so that the ratio of the two is independent of the slit's breadth. Now, we can certainly say that the amount of radiation reflected must be less than $E_\lambda\delta\lambda$, for this is the whole amount of radiation of reflectable wave-length that falls on the crystal. So we have as an upper limit to the reflexion an amount $E_\lambda\lambda \cot\theta\,\delta\theta \Big/ \int_0^\infty E_\lambda d\lambda$. In this all quantities are definite except $\delta\theta$, and to get the best upper limit we want to know how small this may be taken. The value of $\delta\theta$ was fixed in D I by the condition that it was to be the smallest value which would not markedly alter the conditions of the experiment. It was shown (p. 323) that with the actual experimental arrangements, if the slit was less than about 5″ broad, the intensity of the reflexion would suffer on account of diffraction, and so this was the value chosen. It would really have been possible to modify the argument so as to make $\delta\theta$ far smaller, for, in fact, the incident radiation would have suffered in the same way as the reflected, but the argument would be complicated because each part of $\int_0^\infty E_\lambda d\lambda$ would be affected to a different extent. Thus the angle $\delta\theta$ was chosen at 5″, because this was the smallest value which would be admissible without markedly altering the experiment. It was quite sufficiently small, as it gave an upper limit about 1/10 of the actually observed radiation. It was this fact that showed that it was wrong to neglect the interactions of the atoms, and led to the investigations of D (II).

The second argument deals with the formulæ for a perfect crystal, and is much simpler. We have seen that the reflexion is perfect in a region of a few seconds of arc, and that this region is responsible for three-quarters of the whole reflexion.

It is necessary, of course, to carry over the calculation so as to deal with white radiation ; but this is quite straightforward, and the argument goes as before, but now with four-thirds of the angle of perfect reflexion taken as $\delta\theta$. Again, it was found that the reflexion was ten times as great as it should be.

Since in both cases the difficulty depended on the exceedingly narrow angle of the reflexion, it was obvious that it could only be met by increasing this angle, and that could only be done by supposing the crystal imperfect, so that there would be several reflexions.

Mathematical Note.

In D(III), p. 814, a rather complicated integral occurs in connexion with primary extinction, which happens to simplify in a remarkable way. The formal proof was not found until the paper was in the press, and so could only be given shortly in a footnote. It is not easy to follow, and we take this opportunity to give a more detailed proof.

Omitting certain factors which are mathematically irrelevant, the integral is

$$\mathrm{I}=\int_{-\infty}^{\infty}\frac{du}{\left|iu+\sqrt{q^2-u^2}\coth m\sqrt{q^2-u^2}\right|^2}.$$

The second term in the denominator is single valued, and is real whether q or u is the greater. Hence we write the integral as

$$\mathrm{I}=\int_c\frac{du}{2u}\left\{\frac{1}{u-i\sqrt{q^2-u^2}\coth m\sqrt{q^2-u^2}}+\frac{1}{u+i\sqrt{q^2-u^2}\coth m\sqrt{q^2-u^2}}\right\},$$

where C is a contour following the real axis from $-\infty$ to $-\eta$, then going over a semicircle above the real axis to η, and then following the real axis to ∞, and η is to tend to zero. Now, if we cut the real axis between $\pm q$ and take $\sqrt{q^2-u^2}$ as positive when u is pure positive imaginary, it is not hard to show that the real part of $\coth m\sqrt{q^2-u^2}$ is always positive above the real axis and negative below. Also $u/i\sqrt{q^2-u^2}$ has its real part positive over the whole plane. Hence the first term in the integrand has no poles

below the real axis, and the second none above. We can thus deform the contour for the second term to infinity above the real axis, and it is easily seen to vanish over the finite arc. The first term can be similarly treated, but in this case it must first be taken across the origin. Thus the integral is altogether equivalent to the integral of the first term taken negatively round a small circle above the origin, and this gives

$$I = \pi \tanh mq/q,$$

which is the required result.

Summary.

The present paper is a review of theoretical and experimental work on the intensity of reflexion of X-rays by crystals. In 1914 Darwin evaluated expressions for the relation between the amount of radiation reflected by a crystal face and the incident X-ray energy. The form of these expressions was shown to depend on the assumptions made as to the interaction between waves scattered in different parts of the crystal. One of these expressions may be applied to the case where a crystal is composed of a mosaic of small blocks, which are only approximately parallel to each other. Moseley and Darwin in 1913, and Compton in 1917, showed that the results of experimental comparisons of incident and reflected energy are of the right order to be accounted for by this formula. W. H. Bragg in 1914 developed an experimental technique for getting comparative measurements of the intensity of reflexion by different faces with the ionization spectrometer. He also first observed the effect of the temperature factor, and showed that extinction took place in the crystals when the rays traversing it were being reflected. His methods of measurement were used by Compton in 1917 and by the authors in 1921, being extended so that an absolute comparison of incident and reflected energy could be made. The other expression for intensity of reflexion evaluated in Darwin's 1914 paper applies to the case of a perfect crystal. Ewald in 1917 attacked the problem of the diffraction of radiation by a perfect crystal, and arrived independently at the same results. Reflexion from a crystal face is shown to be perfect over a small range of glancing angles, the extent of which is proportional to the efficiency with which each crystal plane reflects the radiation. In a series of papers (Bragg, James,

and Bosanquet, 1921) quantitative measurements were made on sodium chloride which supported the accuracy of the formula for the mosaic crystal, and led to a determination of the scattering powers of sodium and chlorine over a wide angular range.

These results were discussed in a paper by Darwin in 1923, and a more complete theory of reflexion by the imperfect crystal was developed. Recently (1925) Ewald has drawn attention to the fact that results obtained with some crystals (calcite, diamond) appear to support the type of formula which applies to a perfect crystal rather than that which applies to the imperfect mosaic. In particular, Ewald discusses a series of measurements on diamond made by W. H. Bragg.

In this paper we have discussed the evidence as to the nature of crystals. This question must be decided before quantitative analysis can be applied, and one may hope for two interesting results from successful analysis. In the first place, it would lead to a knowledge of the scattering power of the atoms, which would be the most direct evidence we have as to the distribution of electrons in the atom. In the second place, in analysing crystal structure we need to know both the scattering power of the atoms and the type of formula which applies to the reflexion. As Ewald has pointed out, the formula for the perfect crystal makes the intensity of reflexion proportional to the structure amplitude. The formula for the imperfect crystal, on the other hand, makes the intensity proportional to the square of the structure amplitude, and this is the relation generally assumed in analysis. We find that most crystals are of the imperfect rather than of the perfect type, but their perfection is sufficiently high to make it necessary to modify the mosaic formula. These modifications take the form of corrections for primary and secondary extinction in the crystal, examined by Darwin in 1923 and further discussed in the present paper. A series of examples are given in which the observed intensities may be compared with those obtained by the two formulæ for the perfect and for the mosaic crystal respectively.

LXXXII. *On Professor Joly's Theory of Earth History.* *By* Harold Jeffreys, *M.A., D.Sc., F.R.S.* *

1. In his book 'The Surface History of the Earth' and in several previous papers Prof. J. Joly has offered a far-reaching theory of the thermal history of the Earth and its geological consequences, based on the hypothesis that so much heat is generated in the interior by radioactivity as to lead to widespread fusion. Some of the fundamental data of his discussion, however, appear to be very questionable, and at several subsequent stages it is doubtful whether the consequences would be those inferred by Prof. Joly.

The initial assumption is that the thickness of the granitic layer of the continents is about 30 km.; three independent lines of argument seem to point to such a value. The whole of the subsequent development depends on this supposition, which therefore requires careful scrutiny. It must be pointed out that two of the estimates are really upper limits, while the other is an order of magnitude; none of them can be regarded as a measure.

The first estimate is obtained by finding the heights of granite and basalt columns that would give isostatic balance together with the observed difference in mean level between the continents and the oceans. There is, however, strong reason for believing that another material besides granite and basalt is involved. The velocity of compressional elastic waves in the upper crust is about 5·4 km./sec., agreeing with what we should expect from laboratory measures on granite under pressure. But all compressional waves that penetrate below the granite layer show a velocity of at least 7·2 km./sec. †, which is substantially greater than the velocity appropriate to basalt or diabase under the pressures involved, but agrees with experimental knowledge for peridotite; dunite gives 7·4 km./sec. ‡. There is no direct seismological evidence of the existence of basalt below the continents, and the basaltic layer may therefore be fairly thin; but the lower layer must consist of a denser and more rigid material extending to a depth of some hundreds of kilometres. It is natural to identify this with peridotite, of density 3·4, or with some still denser material. This

* Communicated by the Author.

† Knott, from the Zöppritz-Turner tables, gives 7·18 km./sec.; other writers give 7·8–8·0 km./sec. *Cf.* B. Gutenberg, *Der Aufbau der Erde*, p. 97.

‡ E. D. Williamson and L. H. Adams, J. Frank. Inst. cxcv. pp. 475–529 (1923).

material is at least as likely as basalt to constitute the suboceanic material that balances the continents, and if so the depth of the granitic layer need only be about 16 km.

The second estimate, due to Oldham, is based on the distance from the epicentre where the P and S phases of a seismic disturbance become distinct; but this involves numerous complicating factors, and can hardly be considered to give more than an order of magnitude. On the other hand, the velocities of Love waves indicate a thickness of about 15 km.*.

The third estimate is based on the fact that the radioactivity in 30 km. of granite in a steady thermal state would just supply the heat that is being conducted out of the Earth. But the apparent agreement would break down if some of the heat rising to the surface is due to the original heat of the Earth, and this may well be appreciable. Thus this estimate is an upper limit to the thickness of the granitic layer.

2. The basic rocks below the granitic layer also contain radioactive matter, and it is upon the heat generated in them that Prof. Joly relies for his main object, which is to explain periodic variation of temperature within the crust. Now there are many soluble problems involving the steady supply of heat to a conducting solid with an outer boundary at a constant temperature, but they all have a common property, namely, that the temperature distribution tends asymptotically to a steady state; there is no possibility of periodicity. The reason for this may be understood by considering the one-dimensional flow of heat in a finite depth of uniform material.

The differential equation satisfied by the temperature V is

$$\frac{\partial V}{\partial t} - h^2 \frac{\partial^2 V}{\partial x^2} = \frac{P}{c\rho}, \quad \ldots\ldots (1)$$

where t is the time, h^2 the thermometric conductivity, x the depth, P the rate of supply of heat per unit volume, regarded as a function of x, c the specific heat, and ρ the density. The terminal conditions we may suppose to be that $V = 0$ at the ends $x = 0$ and $x = l$. Then (1) and the terminal conditions are satisfied if $V = V_0$, where

$$V_0 = -\int_0^x \int_0^{\xi_1} \frac{P(\xi_2)}{c\rho h^2} d\xi_1 \, d\xi_2 + \frac{x}{l} \int_0^l \int_0^{\xi_1} \frac{P(\xi_2)}{c\rho h^2} d\xi_1 \, d\xi_2. \quad (2)$$

We have also an initial condition that V differs from V_0 by

* Jeffreys, M. N. R. A. S. Geoph. Suppl. 1, pp. 282–292 (1925).

V_1, say, when $t=0$; V_1 can be expressed in a sine series of the form

$$V_1=\sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Then all the conditions are satisfied if

$$V=V_0+\sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{l}\, e^{-k^2n^2\pi^2t/l^2}, \quad . \quad . \quad . \quad (4)$$

which tends continuously to V_0 as the time increases. The time inevitably enters through negative exponential factors and not through trigonometrical ones.

Prof. Joly's theory introduces two complications designed to avoid this result, but it may be questioned whether they succeed. The first is to suppose that a layer below the crust becomes liquid. The probable course of events in this case may be inferred from an analogue, which is easier to visualize than the thermal problem. If a stretched string in a viscous liquid, with the ends fixed, is slightly displaced from the position of equilibrium, its equation of motion is

$$\lambda\frac{\partial^2\eta}{\partial t^2}+k\frac{\partial\eta}{\partial t}-T\frac{\partial^2\eta}{\partial x^2}=F, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

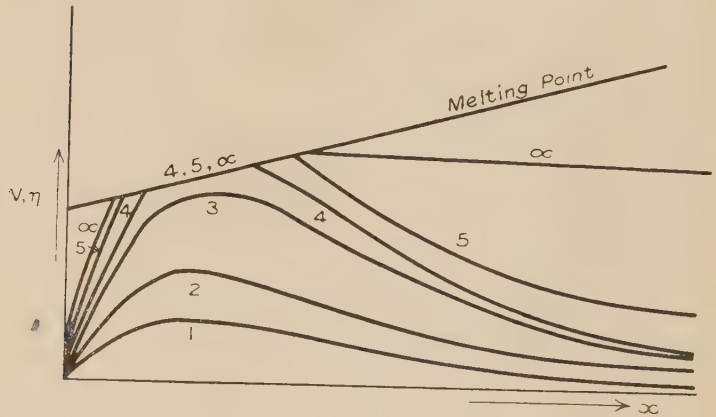
where η is the transverse displacement, λ the mass per unit length, k a constant depending on the viscosity, T the tension, and F the transverse force per unit length. If the motion is slow enough, or the viscosity high enough, the first term becomes negligible in comparison with the second, and the equation is indistinguishable from that for heat conduction. So long as the medium in the thermal problem is solid, therefore, there is a corresponding problem of a string, whose solution will give at once the complete solution of the thermal problem. The absence of periodicity from the motion of a string with very high damping is in accordance with ordinary experience.

When fusion occurs anywhere, the excess of the heat generated over that conducted away produces no further rise of temperature until the change of state there is complete. Afterwards convection will raise the new heat generated to the bottom of the still solid material, and thus fusion will gradually extend upwards. In the analogue of the string, the conditions of fusion will correspond to a fixed barrier; after an interval, corresponding to the time needed for the change of state, the force originally applied to the constrained region is transferred to its upper margin. The constrained region will extend until the gradient at the end is such that the transverse component of the tension there just

balances the whole of the applied force. No further change will occur.

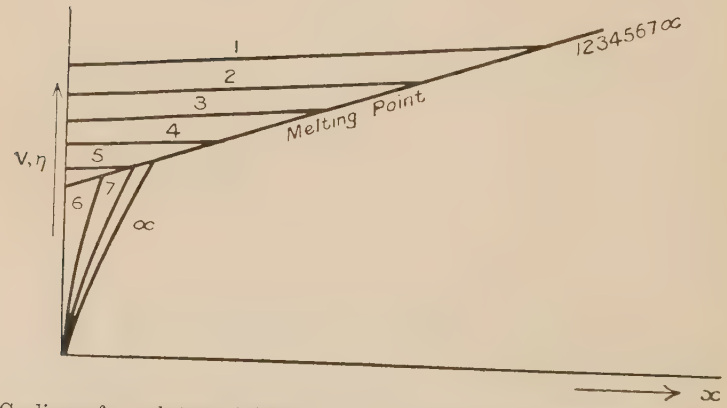
The above argument is qualitative, but appears plausible, and could be tested by experiment if desired. The course of the changes is given by the successive curves in fig. 1. The scale of η is, of course, much exaggerated.

Fig. 1.



Heating of an initially cold solid.

Fig. 2.



Cooling of a substance initially fluid. Curves show successive states; those marked ∞ denote the ultimate steady states. The figures are believed to be qualitatively correct, but are not the result of calculation.

If the material is originally fluid, but is denser when solid than when fluid, the corresponding curves are as in fig. 2. In neither case does there seem to be any reason for assuming periodicity in the solution.

3. In the case of the Earth several cases may arise. Permanent solidification may occur everywhere, which is the view that I believe and have developed elsewhere; fusion may occur below the continents and not below the oceans; or fusion may occur below both continents and oceans. Prof. Joly adopts the last alternative, but not for any obvious reason. Even if we accept his view that continental conditions imply fusion temperatures at depths of the order of 30 km., there is every reason to suppose that the basic rocks of the ocean floor are much less radioactive, so that fusion may well fail to occur below the oceans. In that case the only effect of fusion below the continents would be to lift the continents up; there is no opportunity for movement into, or out of, the continental regions, and mere vertical expansion in fusion would not disturb isostasy.

Prof. Joly, however, assumes that at intervals the whole subcrustal region, below continents and oceans alike, becomes fluid, but that the surface rocks remain permanently solid. Tidal friction is then supposed to tow the crust around over the fluid layer, and the crust below the oceans is supposed to be much thinner than that below the continents. In these conditions rapid heat conduction through the suboceanic crust is supposed to restore solidity. It must be pointed out, however, that the melting points of rocks increase with the basicity; so oceanic rocks must, on the whole, have higher melting points than continental ones. If the crust below the oceans is thinner than that below the continents, it follows, on both grounds, that the rate of outflow of heat through the ocean floor in the equilibrium state is much greater than that below the continents. Thus a greater supply of heat is needed below the oceans; whereas every previous consideration points to the greater supply of heat by radioactivity taking place below the continents.

This contradiction appears to arise from the statements on pp. 102–3 of Prof. Joly's book. "If (the substratum) is solid, the radioactive heat continually being developed . . . beneath the continents is almost entirely accumulated." "The blanketing effects of continental radioactivity . . . effectively block its escape by conductivity." It seems to be supposed that heating a region prevents the transmission of heat through that region; which is not the case. The equation of heat conduction being linear, the effects of all sources of heat are purely additive; radioactivity within the granitic layer can do absolutely nothing to prevent the transmission to the surface of the heat developed below, and only ensures that the temperatures below that layer become higher than they would in its absence.

Prof. Joly then supposes that solidity is restored everywhere by conduction through the ocean floor. But it seems that even if the crustal thickness varies in the way postulated by Prof. Joly, the only effect of the revolution of the crust would be to make the temperature distribution oscillate about a mean, this mean being nearly what would result if radioactivity at every depth were a mean of the values appropriate to land and sea conditions, weighted according to the area involved. If fusion in the steady state was involved below both land and sea, there seems no reason to believe that alternation between land and sea conditions will restore solidity; it seems much more likely, in view of the above considerations, that after any transition the temperature distribution would tend asymptotically towards the equilibrium conditions in the new circumstances; the depth of fluid everywhere would then always be between the values appropriate to continental and oceanic conditions.

4. There is a further difficulty in making the crust revolve at the required rate. Tidal friction is appealed to for this purpose; but it is well known that perfect fluidity on an extensive scale in a crustal region is likely to abolish the ocean tides altogether. A thin crust of any reasonable rigidity is so flexible that it opposes an insignificant resistance to tidal deformation of a fluid layer more than a few kilometres deep below it *, and its outer boundary therefore remains almost an equipotential surface throughout the tidal motion. There is therefore no force tending to move the ocean along the boundary, and there can be no ocean tides. The magma layer being itself a perfect fluid, there can be no dissipation of energy within it, and there is therefore no tidal friction.

Passing to the case of infinite viscosity in the intermediate layer (that is, perfect elasticity) we may have tidal friction in the ocean, but it cannot produce any permanent displacement of the crust. Permanent deformation of the crust, in fact, requires a rather delicate adjustment of conditions. Intermediate viscosities will give oceanic tides, and the tides in the magma layer will also lag; both effects will give tidal friction, the latter being capable of giving the greater values on account of the higher density of the matter involved.

Let us then investigate the tides in a thin viscous fluid layer just below the surface. The outer crust is supposed thin enough to offer negligible opposition to the motion of the fluid, so that the upper boundary of the fluid will be

* Love, Proc. Roy. Soc. (1908).

treated as free. The long wave approximation, that the variations of pressure are independent of the depth, will hold; also the depth considered by Prof. Joly, 100 km., is great compared with that which gives inversion of phase in the tides, so that the acceleration terms also will be negligible. The motion may then be treated as approximately laminar, and the equations of motion reduce to

$$\nu\frac{\partial^2}{\partial z^2}(u,\ v)=\frac{g}{a}\left(\frac{\partial}{\partial\theta},\frac{\partial}{\sin\theta\partial\phi}\right)(\zeta-\bar{\zeta}) \quad . \quad . \quad . \quad (1)$$

in Lamb's notation. If h be the depth, the horizontal velocities must be proportional to $2hz-z^2$, where z is measured upwards from the bottom of the layer; whence

$$(u,\ v)=-\frac{g}{2\nu a}(2hz-z^2)\left(\frac{\partial}{\partial\theta},\frac{\partial}{\sin\theta\partial\phi}\right)(\zeta-\bar{\zeta}). \quad . \quad (2)$$

The equation of continuity is

$$\frac{\partial\zeta}{\partial t}=-\frac{1}{a\sin\theta}\int_0^h\left[\frac{\partial(u\sin\theta)}{\partial\theta}+\frac{\partial v}{\partial\phi}\right]dz, \quad . \quad . \quad . \quad (3)$$

$$=\frac{gh^3}{3\nu a^2\sin\theta}\left[\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}(\zeta-\bar{\zeta})\right\}+\frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}(\zeta-\bar{\zeta})\right]. \quad (4)$$

Now ζ and $\bar{\zeta}$ are surface harmonics, of order n say, so that

$$\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}(\zeta-\bar{\zeta})\right\}+\frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}(\zeta-\bar{\zeta})$$
$$=-n(n+1)\sin\ (\zeta-\bar{\zeta}) \quad . \quad . \quad (5)$$

Hence

$$\frac{\partial\zeta}{\partial t}=-\frac{gh^3}{3\nu a^2}n(n+1)(\zeta-\bar{\zeta}). \quad . \quad . \quad . \quad . \quad (6)$$

But $\bar{\zeta}$, the height of the equilibrium tide, is affected by the mutual attraction of the fluid. If the part due to the moon is ζ_0, we have

$$\bar{\zeta}=\zeta_0+\frac{3}{2n+1}\frac{\rho}{\rho_0}\zeta, \quad . \quad . \quad . \quad . \quad (7)$$

ρ and ρ_0 being the surface-density and the mean density of the Earth. Then

$$\frac{\partial\zeta}{\partial t}=-\frac{gh^3}{3\nu a^2}n(n+1)\left[\zeta\left(1-\frac{3}{2n+1}\frac{\rho}{\rho_0}\right)-\zeta_0\right], \quad . \quad (8)$$

and if the time factor is $e^{\iota\gamma t}$

$$\frac{\zeta}{\zeta_0}=\frac{n(n+1)gh^3/3\nu a^2}{\iota\gamma+n(n+1)\left(1-\frac{3}{2n+1}\frac{\rho}{\rho_0}\right)\frac{gh^3}{3\nu a^2}} \quad . \quad . \quad . \quad (9)$$

Tidal friction is a maximum if the phase lag is $\frac{1}{4}\pi$, when

$$n(n+1)\left(1-\frac{3}{2n+1}\frac{\rho}{\rho_0}\right)\frac{gh^3}{3\nu a^2}=\gamma. \quad . \quad . \quad . \quad (10)$$

In the case of the semidiurnal tide $n=2$, $g=981$ cm./sec.^{2}, $1-\frac{3}{2n+1}\frac{\rho}{\rho_0}=0{\cdot}6$, $a=6{\cdot}37\times10^8$ cm., $\gamma=14\times10^{-5}$/sec. Prof. Joly takes $h=10^7$ cm. Then

$$\nu=2{\cdot}2\times10^{10}\text{ cm.}^2/\text{sec.}$$

gives the maximum frictional couple. The ratio of the amplitudes of ζ and ζ_0 is $\left(1-\frac{3}{2n+1}\frac{\rho}{\rho_0}\right)^{-1}2^{-\frac{1}{2}}=1{\cdot}2$.

The frictional couple is *

$$\mathrm{N}=\frac{32\pi}{15}ga^2\rho\lambda q^2\sin 2\epsilon, \quad . \quad . \quad . \quad . \quad (11)$$

where q is the maximum amplitude of ζ_0, λq that of ζ, and 2ϵ the phase difference. Now if the outer shell is rotated over the interior with relative angular velocity ω, the relative velocity at the top and bottom of the fluid layer is $a\omega\sin\theta$, and the rate of shear $a\omega\sin\theta/h$. The shearing force is therefore $\nu\rho a\omega\sin\theta/h$, and the couple required is

$$\begin{aligned}\mathrm{N}&=\int\int\frac{\nu\rho a\omega}{h}\sin\theta\,.\,a\sin\theta\,.\,a^2\sin\theta\,d\theta\,d\phi\\&=\frac{8}{3}\pi\frac{\nu\rho a^4}{h}\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)\end{aligned}$$

From (11)

$$\mathrm{N}=4\times10^{24}\text{ gm. cm.}^2/\text{sec.}^2,$$

approximately; so that

$$\mathrm{N/C}=5\times10^{-21}/\text{sec.}^2,$$

where C is the Earth's moment of inertia. The present value is about 2×10^{-22}/sec.^{2} Also

$$\omega=6\times10^{-16}/\text{sec.}$$

Thus it would take $1{\cdot}6\times10^{15}$ secs., or 5×10^7 years, to displace an equatorial continent relative to the interior by 6000 km. This estimate of the time requires a further increase for three reasons. The yielding of the solid interior

* *Cf.* Jeffreys, 'The Earth,' 14·21 (6) and (10).

will reduce the tides in the fluid layer, thereby at least halving ω; in the above discussion the upper surface has been supposed free, so that the velocities are overestimated; and the whole couple has been supposed applied to the enclosing shell, whereas actually it would be distributed through the fluid, giving a correspondingly slower displacement. Prof. Joly requires such a displacement to occur in 3×10^6 years, and for this purpose, on his own numerical assumptions, tidal friction is inadequate.

Reducing the viscosity below 2×10^{10} cm.^{2}/sec. will reduce the tidal friction, but the rate of crustal displacement will not be greatly affected, since it depends on $(\sin 2\epsilon)/\nu$, which remains finite when ν tends to zero.

The discordance could be reduced by reducing the assumed value of h; for the optimum value of λ is proportional to h^3 and the associated ω to h/ν or h^{-2}. Reducing h to 20 km. would make it just possible to make this part of the theory self-consistent; but it is still necessary for viscosity throughout the displacement not to exceed considerably the value necessary to give the maximum tidal friction. Further, with a fluid layer of such a depth it is possible that the deeper projections on the under side of the outer layer would touch the bottom of the fluid layer and prevent all motion; and the reduction of the depth of the fluid would much reduce, and perhaps annihilate, the volume changes available for geological purposes.

5. To sum up, Prof. Joly's theory requires:—

(*a*) That the granitic layer of the continents should be about 30 km. thick, leading to fusion below it on account of excess radioactivity;

(*b*) That if fusion occurs, the upper solid layer should be much thinner below the oceans than in the continents;

(*c*) That tidal friction in such conditions should make the outer shell rotate with respect to the interior;

(*d*) That the result of such rotation should be to restore solidity in the liquefied layer.

If any one of these assertions is incorrect, the theory will fail. Reasons are given here for believing that all are incorrect. The estimate in (*a*) is probably excessive; the arguments for (*b*) are erroneous; with Prof. Joly's conditions tidal friction is not adequate for the purpose of (*c*); and, contrary to (*d*), fusion once initiated seems likely to be permanent.

LXXXIII. *The Surface History of the Earth.* *By* J. Joly, *F.R.S.**

IN his criticism of my theory of the surface history of the earth, Dr. Jeffreys commences with the statement that "the initial assumption is that the thickness of the granitic layer of the continents is about 30 km. . . . . The whole of the subsequent development depends on this supposition. . . . ."

Dr. Jeffreys's deduction is entirely mistaken. If the assumption of 30 km. is seriously wrong, one or other of two cases must arise. Radioactive heat derived from the upper part of the substratum would share in maintaining the surface gradient, or radioactive heat derived from continental rocks would flow downwards into the substratum. It is not improbable that the first condition arises in the case of so shallow a continent as Europe The second case, as I have elsewhere pointed out (Phil. Mag. July 1923), probably arises in the case of parts of S. Asia. The very unequal thickness of the continents is pointed out in 'The Surface History of the Earth,' p. 53.

In this matter there is obviously latitude in the choice of data. In earlier estimates I arrived at 24 km. (Phil. Mag. June 1923). I think I have more than once pointed out that the principal teaching of such estimates is that the substratum beneath the continents must be near its melting-point, and that but little heat can be escaping from it, the major part of that which arises out of the surface gradient being ascribable to the continental rocks themselves.

Dr. Jeffreys, having concluded that a thinner continental crust than 30 km. must be fatal to the radioactive theory of surface history, then proceeds to show from certain seismic data that this crust must be about 15 km. thick. As I have said, the point is not of serious importance. However, it is of interest to note that so careful a writer as Dr. A. Holmes draws a different conclusion out of his examination of the available data, and adds: "Jeffreys concludes that the thickness of the granite shell is between 10 km. and 30 km., and favours an estimate of 15 km. This I believe to be an under-estimate, even on his own data. I would prefer to adopt limits of 25 and 30 km. as more probable, particularly as the important work of

* Communicated by the Author.

Mohorovičić lends support to estimates even higher than 30 km."*

On the basis of the mean continental elevation over sea-level and the mean depth of the ocean, and assuming that the continents are granitic and float isostically in a basaltic substratum the surface of which is the ocean-floor, we arrive at a mean continental depth of 30·7 km. This is, I believe, the most direct estimate we possess. (Surf. Hist. of the Earth, p. 35.)

Dr. Jeffreys then argues for the existence of a peridotic layer beneath the continents, with a possible thin layer of basalt intervening. He considers that this would harmonize with the velocity of compressive seismic waves which penetrate below the continents. He states that all such waves penetrating below the granitic layer show a velocity of at least 7·2 km. per sec. Now, there is much that is precarious about seismic evidence, and in this case there are quite contrary deductions available. Thus, Mohorovičić (*Beit. zu Geophysik*, 1913 & 1914) gives the average velocity of compressional waves in the outer 60 km. of the continental lithosphere as 5·8 km. per sec. Recent work upon the elastic constants and densities of rocks would go to show that at a depth of 35 km. the velocity in granite would be 5·9 km. per sec. Here there is evidently contradiction not only to the assumption of the existence of a peridotic layer immediately beneath the continents, but also to the shallow continents assumed by Dr. Jeffreys. Beyond 60 km., however, the velocity increases to 7·9 km. This—as Holmes points out (*loc. cit.* p. 531)—also agrees with the velocity given in Knott's table.

There is, evidently, very slender evidence for the view that close under the granitic continents peridotite exists. The Oppau explosion-wave supports the view that "around Oppau the basaltic layer is in place beneath a depth of 30 to 35 km." (A. Holmes, *loc. cit.* p. 531.) Holmes appears finally to favour the view, but not on any decisive grounds, that the basaltic layer is nowhere more than 42 km. thick, and that a peridotic layer of less radioactivity then begins. The radioactivity of peridotites and of the magma basalts differ a little, the calorific values being in the approximate ratio of 114 : 98 †. And there is some reason to believe they are nearer to equality. The melting-points also seem generally to differ a little, that

* Geol. Mag. Dec. 1925, p. 531.

† Phil. Mag. Nov. 1924.

of peridotite being the higher (it is difficult to say how much); but it is certain that the viscosity of the peridotites extends over a wider range of temperature than is the case with basalts. I have pointed out—more especially in my Halley Lecture (pp. 31–35)—the consequences which may arise from a deep-seated layer of peridotite.

Dr. Jeffreys next proceeds to combat the view "that periodic variation of temperature" arise within the crust; which he describes as my "main object."

Now, this is not at all my main object. If Dr. Jeffreys had stated that my main object was to show that there is periodic accumulation and discharge of heat from within the crust he would be correct. But the heat is latent. There is but little variation in temperature. Throughout the rest of his argument he appears to labour under this initial error, and to assume that the problem he undertakes to discuss is concerned mainly with a periodic variation of temperature gradient; that is to say, the problem is one of thermal conductivity.

"There is," he says, "no possibility of periodicity." This is true of the mathematical theory of heat conduction. The periodicity which I have referred to in all my writings upon this subject arises from the gravitative instability which affects the ocean-floor when an underlying substratum assumes, in consequence of accumulated latent heat, the fluid state, and becomes of less density than the solid floor. The consequences arising out of this condition allow a very great transfer of latent heat by *convection* from the lower to the upper parts of the magma, so that the upward heat-flux during the fluid phase is very much greater than the mean, while the upward heat-flux during the solid phase is very much less than the mean.

The differential equation cited by Dr. Jeffreys is the same as that used by Mr. Cotter in his paper "On the Escape of Heat from the Earth's Crust" (Phil. Mag. Sept. 1924), save that he assumes P (the rate of supply of heat per unit volume) constant. Of course the time enters through a negative exponential factor. The fact that Dr. Jeffreys thinks that the only way periodicity can arise is by a trigonometrical time factor in the expression for conduction, shows that he is under a misconception as to the conditions involved in the theory.

The analogue of the string damped by a viscous liquid is misleading. He supposes a barrier to limit the displacement of the string, just as the melting-point limits the rise of temperature of a solid. But he has nothing

analogous to the accumulation of energy in the form of latent heat. Also, there is nothing corresponding to the transfer of this energy by convection; *i. e.*, the precipitation of solid basalt at the bottom of the fluid region accompanied by the melting away of the floor above. In his figure Dr. Jeffreys makes the temperature diminish with depth, just as the amplitude of vibration of a string diminishes towards the fixed end.

Following this, Dr. Jeffreys says that I adopt the view that fusion occurs below the ocean and below the continents, "but," he says, "not for any obvious reasons." This and the sentence which follows suggest that not alone is he under a misconception as to the nature of the theory in some of its most important aspects, but he has not entered quantitatively into the physical data brought forward where such are available. We are here, *inter alia*, informed that "the melting-points of rocks increase with their basicity; so oceanic rocks must, on the whole, have higher melting-points than continental ones." This is, however, inconsistent with the facts.

From my book (pp. 102–103) I am quoted as follows:— "If the substratum is solid, the radioactive heat continually being developed beneath the continents is almost entirely accumulated." "The blanketing effects of continental radioactivity . . . effectively block its escape by conductivity." Surely the meaning is plain enough; and is expounded many times throughout the book! Nevertheless, here is Dr. Jeffreys's comment:—"It seems to be supposed that heating a region prevents the transmission of heat through that region; which is not the case." We seem to have here the mathematical point of view with a vengeance. It is quite true that the linear character of the differential equation of heat conductivity suggests that a more correct way of stating the case would be to define that the flux of heat through the bottom of a continent is the algebraic sum of (*a*) the downward heat-flow from a radioactive continent into a non-radioactive substratum, and (*b*) the upward heat-flow from a radioactive substratum into a non-radioactive continent. I preferred, however, to take refuge in the second law of thermodynamics!

In the next paragraph Dr. Jeffreys seems to have become involved in a fresh difficulty. He says: "There seems no reason to believe that alternation between land and sea conditions will restore solidity." The restoration of solidity is not attributed to this, but to the precipitation of solid at the bottom of the fluid magma, together with

rise of superheated fluid magma which melts away the crust below the ocean-floor, thus transferring an enormous amount of (latent) heat by convection which escapes rapidly through the attenuated crust by conduction, and even by partial break-up of the ocean-floor. The temperature of the ocean waters remains, however, almost unaffected (*loc. cit.* pp. 98, 99).

Coming now to that part of Dr. Jeffreys's paper dealing with certain tidal effects which may be expected to arise upon the melting of the substratum, we find in his able treatment of this difficult subject a contribution to the surface history of the earth which, if confirmed, will have added considerably to our knowledge.

Dr. Jeffreys shows that conditions of depth of substratum as well as of its viscosity exert a controlling influence upon movements of the surface crust. That is, such movements as are to be expected as the effects of tide-generating forces acting upon the tidal prominences existing at opposite sides of the earth. He finds that, with the assumption of a depth of fluid substratum of 100 km. and favourable assumptions as to viscosity, an adequate displacement of the continents and ocean-floor over the substratal surface could be expected to take place only in some 50 million years. However, if the depth be taken as some 20 km. and the viscosity not greatly different from that giving the maximum tidal friction, it is possible that this part of the theory is self-consistent.

Of course the discussion applies to existing conditions of lunar proximity. Far greater tide-generating forces—according to Darwin's theory of lunar history—must have operated in the past, and very possibly affected the earlier terrestrial revolutions with which we are acquainted.

It would appear that the principal addition to our knowledge here involved is in the deduction that when solidification of the substratum is progressing, the shifting of the outer crust takes place effectively when the substratum has shallowed to a depth of about 20 km. Loss of heat will then have been in progress, according to my assumption as to its total effective depth, for a considerable time. This fact, as well as the pressure conditions, must influence the prevailing condition of viscosity which, however, we cannot determine, but which we are entitled to assume as favourable, having regard to what we know of geological history.

Even if we assumed that there were no other means

of equalization of thermal conditions beneath oceans and continents, it would appear that the crustal shift must ultimately account for complete equilibrium; for the gradual shallowing of the suboceanic depths must in itself involve continued approximation towards optimum conditions of crustal movement. This in turn involves progressive thermal equalization beneath continents and oceans, and thus introduces another accelerative factor. Plainly the results arrived at by Dr. Jeffreys involve an accelerative approach, slow at first, towards optimum conditions.

There are, however, other sources of magmatic circulation between sub-continental and sub-oceanic regions. Tidal movements must promote such circulation. I have referred to this in earlier papers upon this subject. Lateral currents have to feed the tidal prominences. Twice diurnally these movements occur; and as it seems probable that the greater, and less rigid, ocean-floor yields most to the tidal forces, very considerable movements drawing upon sub-continental magma may be expected to occur. Again, attending the slow sinking of the continents arising out of loss of magmatic density, a considerable transfer of sub-continental magma must continually be taking place.

Still another source of circulation, purely gravitational and arising out of the great vertical magmatic circulation beneath the oceans, seems to be inevitable. I refer to an attendant lateral circulation arising out of the gain in density of magma giving up latent heat to the ocean-floor. As this sinks downwards an upper lateral inflow of lighter material from beneath the continents will arise. At the lower levels compensatory magma, displaced by descending solidified basalt from above, flows from sub-oceanic to sub-continental regions.

A somewhat similar circulation takes place to-day in the oceans. We find, in fact, the cold waters of the Polar Regions spreading over the entire floor of the oceans. What is more, these currents extend over distances much in excess of the substratal circulation we have been considering; for it is known that the source of the cold bottom layer in the ocean is almost entirely of Antarctic origin, and penetrates to high north latitudes both in the Pacific and in the Atlantic. That such a great current exists is proved from the fact that, although exposed to sources of heat both above and beneath, the low temperature is

perennially maintained*. This circulation is purely gravitational, and arises out of thermal changes of density. The circuit is closed through reverse surface currents and also by evaporation in the Tropics and precipitation in high latitudes.

We perceive, therefore, that while Dr. Jeffreys's conclusion leads us to a closer recognition of all the conditions, it raises no difficulties in the physical basis of the theory.

The grounding of compensations attending an east to west motion of the crust under tidal forces, towards closing stages of cooling, has been referred to by Dr. H. H. Poole as possibly affecting mountain-building (Phil. Mag. Sept. 1923). These effects would not be expected to interfere with crustal shifting at depths at all comparable with 20 km.—as Dr. Jeffreys suggests; for, in fact, mountain-genesis is, at this time, still in its earlier stages, and, of course, the compensations of a previous continental epoch will, to a large extent, have vanished. To-day we have to reckon with great compensations. But how much of these will remain in 30 or 50 millions of years? We have to bear in mind that it is an old and much denuded earth which the revolution assails.

When continental shifting finally ceases and tidal disturbances die out due to shallowing of the fluid substratum, there may remain, possibly, some local unconsolidated magma both under oceans and under continents. Slow escape by conductivity through the overlying crust accounts for such lodgments †.

I do not think we are faced with any difficulties in accounting for such depths of subcrustal fluidity as I have assumed. Lesser revolutions may arise out of lesser depths of liquefaction. Greater revolutions may arise out of greater depths of the substratum, and with these last the accumulated radioactive energy in a peridotic layer may be involved, as I have pointed out in my Halley Lecture. The new knowledge arising out of Dr. Jeffreys's analysis does not affect the available mountain-building forces and displacements attending a great revolution.

There is very striking geographical evidence for a westerly drift of the continents during some previous period of subcrustal fluidity. It is best seen where the westerly margin of the Pacific meets the easterly margin of Asia. Now, if the outer crust of the earth, retained

* Supan, 'Grundzüge der Physischen Erdkunde,' p. 358.

† 'The Surface History of the Earth,' p. 95.

by lunar attraction, had moved from east to west relatively to the substratum, the sub-Asiatic substratum must have been displaced beneath the Pacific margin. The greatest continental stretch upon the globe lies to the west. If the molten substratum underlying this great continent was for ages being traversed by Eastern Asia and the adjacent Pacific floor, some evidence of exceptional thermal conditions might be expected.

Coming now to the geologic structure of this region, we find great slices of the Eastern Asiatic margin faulted downwards along step faults parallel with the coast and apparently conditioning the delimitation of the Japanese Islands. Many geologists consider the shallow Japanese Sea as due to foundering of an intermediate crustal area. Seaward we find the ocean-floor traversed by some of the greatest deeps on the globe. The whole region is continually shaken by earthquakes and by volcanic forces. It is to-day the most restless part of the earth's surface.

Now, foundering of continental land can only be explained in *one* way—having regard to isostasy—and that is by the melting away of underlying compensations. This view provides at once an adequate explanation. In this case the foundering of much of the fragmented coast and the buckled ocean-floor alike point to an area which had been undermined by extreme thermal conditions. Contrast with it the features of the eastern shores of the Pacific. There we find every sign of a strong ocean-floor. There is no continental fragmentation: the volcanicity and coastal oscillations are of different origin and are associated with mountain-building. There are no great deeps ranging along the continental margin. Nearly all the volcanic islands of the Pacific are in its western half. So are the fracture lines or rifts which seem to have determined the alignment of the Oceanic Islands.

The Atlantic offers no such remarkable conditions. There is a relatively small continental area lying to westward of the ocean. However, there were formerly highlands extending the east coast of North America into the Atlantic—highlands responsible for the enormous volume of sediment which built up the Appalachian Ranges. But ancient Appalachia for the greater part foundered long ago. There is no better attested case of foundering in geological history. We can assign the source if we reconstruct the past in the light of the radioactive surface history of the Globe.

LXXXIV. *The Sodium Arc in a Vacuum.* *By* F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College, Exeter* *.

[Plate XIV.]

1. *Introduction.*

THE spectrum lines emitted from any arc operated in a vacuum are very narrow, as distinct from the broadened and reversed lines given by the arc in air at atmospheric pressure. Unfortunately, with a number of substances the vacuum arc is intermittent even at potential differences as high as 200 volts. Rayleigh † has described a satisfactory type of sodium vacuum arc lamp made of silica in which the vapour is generated by the continuous heating of a pool of the metal forming the cathode, the anode being a tungsten rod. While working with a modified form of sodium arc lamp, it was found that under certain conditions the heat from the arc itself was sufficient to produce enough vapour for the discharge, no preliminary heating being required.

The main features of this lamp are shown in fig. 1. It is made of soda glass with windows at D and C. The cathode A consists of a pool of sodium metal in a glass tube, through the base of which passes the iron lead-in wire. A clearance between the outside of this cathode container and the inner wall of the lamp ensures that no sodium splutters to the glass walls. If this precaution is not observed, the arc passes by way of the spluttered sodium, and owing to the intense local heating developed, the glass invariably cracks. The anode B is an iron ring, so that the luminous vapour from the arc can be distilled away through the anode. There is a fair clearance between the latter and the glass walls, and no sodium can collect at this clearance. With these precautions it is possible continually to use the lamp without fracture, and such a glass lamp, which can be quickly constructed, is very useful as a source of sodium radiation. An auxiliary electrode E, enabling a momentary electric discharge from an induction coil to be passed between E and B, starts the arc. In actual practice the cathode A was cemented into a glass tube, which could be waxed on to the lower open end of the lamp, so that the sodium in the cathode container

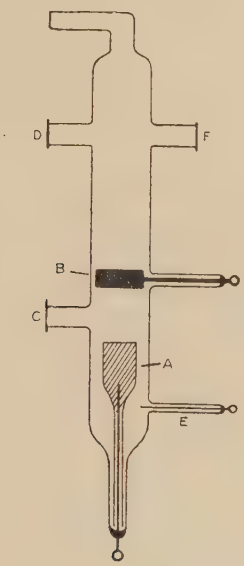
* Communicated by the Author.

† Strutt, Proc. Roy. Soc. A. xcvi. p. 272 (1919).

could be easily and quickly replenished. This waxed joint was so far removed from the actual arc that it was not affected by the heat generated while the lamp was in operation.

The arc can be started by applying a potential difference of 90 volts between A and B, and then passing a momentary electric discharge between E and B. No heating is necessary, but asbestos cloth was wrapped around the lamp, as in the experiments made it was necessary to ensure that

Fig. 1.



the vapour which was being pumped away did not condense before it reached the window D. The current is regulated by a resistance, but the arc does not persist if the current falls below 1·5 amp., and it does not strike if the applied potential difference is less than 90 volts, although after the arc has been started the actual fall of potential across the electrodes is not greater than about 40 volts. No persistent arc could be obtained with the sodium as the anode. In the experiments the lamp was connected to a pump, running continuously, but a good vacuum is maintained while the arc is passing in the absence of the pump.

The spectra were observed and photographed by means of the constant deviation spectrometer.

2. *Experimental Results.*

When the arc is started the sodium vapour pressure is very low, and the radiation emitted is pink in colour. At this stage the luminosity is due to the current passing through the residual gases—chiefly nitrogen, hydrogen, and oxygen, and when examined through the window C the nitrogen bands are very prominent, as shown in spectrogram No. I. (Pl. XIV.). The most prominent lines are those constituting the first group of the positive bands, stretching from λ 6878 to λ 5754, the lines in the second group being extremely faint. The persistence of such a comparatively low voltage arc in the absence of an incandescent electrode is unusual, and must be explained by the small cathode fall of potential at the sodium electrode. It is well known that all of the alkali metals exhibit an abnormally low cathode fall.

Occasionally the whole of the lamp was filled with a brilliant blue "flash," and this luminous gas could be drawn along the tube from the arc, the luminosity persisting for 20–30 cm. along the tube. Unfortunately this "flashing" occurred spasmodically, so that its spectrum, and the conditions for excitation, could not be determined, but it is hoped to investigate the effect later.

After all of the air has been removed, and before the heat from the arc has become sufficient to produce any very appreciable amount of sodium vapour, a little hydrogen remains and is, in fact, extremely difficult to remove. At this stage the pressure within the lamp is very low, the glass walls showing green fluorescence under the action of the electric discharge. The arc discharge, viewed at C, shows a pink-coloured radiation which, when examined, is found to consist mainly of hydrogen lines—in fact, with the exception of λ 5890, λ 5896 from sodium, all the other lines are of the Balmer series, or of the secondary hydrogen spectrum, the outstanding lines being those constituting the first Fulcher band in the red. The second Fulcher band is very faint in comparison. The most intense lines are those in the three series S_1, S_2, and S_3, the lines of these series decreasing uniformly in intensity as they extend towards the red end of the spectrum. This is shown in spectrograms No. II. and No. V. (Pl. XIV.), the latter being an enlarged photograph of the region λ 6565–λ 5680.

It is well known that for a high relative intensity of the secondary hydrogen spectrum purity of the gas is essential, and this spectrum appears under less energetic conditions

of excitation than the Balmer series, the latter alone being found in vacuum tubes excited by powerful condensed discharges. Fulcher * has shown that when hydrogen is excited by the impact of cathode rays, the relative intensity of the secondary spectrum increases as the velocity of the cathode rays is reduced, and the Fulcher bands are developed at these low potentials, the Balmer series lines becoming weaker. The bands are, as a rule, very faint in the presence of impurities, but in the present experiments the bands and the Balmer lines are both very intense in the presence of sodium vapour, although the amount of vapour must be minute at this stage, as the only prominent sodium lines are λ 5896 and λ 5890.

Kiuti †, using an arc at 400 volts between a tungsten anode and a cathode consisting of a bundle of tungsten filaments in an atmosphere of hydrogen at 2-3 atmospheres pressure, found that at high currents the lines of the secondary spectrum above λ 5650 were intense. Fulcher, on the other hand, used only 40 volts, and Merton and Barratt ‡ state that the Fulcher lines are essentially low pressure lines, by which they indicate a pressure at which the walls of the vacuum tube show a vivid green fluorescence.

It has been inferred by various experimenters that the Fulcher lines between λ 6000 and λ 7000 originate in the same type of ionization of the molecule whether complete or partial. The predominance of the red bands over those in the second band suggests that the series in the first and second bands are not due to the same molecular system. On the other hand, in the present work, the series S_1, S_2, and S_3 are more highly developed than the remaining series in the first band—S_4, S_5, S_6, and S_7. This seems to indicate a closer resemblance in origin between S_1, S_2, and S_3, than exists between these series as a whole and the remaining series.

The bands undoubtedly belong to the arc type spectra, and it may be mentioned that in the first spectrogram the band spectrum of nitrogen alone is present. There is no trace of the arc or spark lines of this element.

As the arc in the sodium lamp continues the heat from it vaporizes the sodium. The spectrum of this element appears and becomes predominant as shown in spectrogram No. III. (Pl. XIV.), which was photographed through the window C. In fact, no lines except those belonging to the principal and

* Astrophys. Journ. xxxvii. p. 60 (1913).
† *Phys. Math. Soc. Japan Proc.* v. p. 9 (1923).
‡ Phil. Trans. A. ccxxii. p. 369 (1922).

the two subordinate series of sodium could be detected. Combination lines do not appear, but it must be remembered that the present experimental conditions do not favour the excitation of such lines. Although the D-lines are very intense the lines of the two subordinate series are bright, and it was found that if the current was decreased, *i. e.*, as the temperature of the arc and the vapour pressure were lowered, the yellow radiation changed to a greenish colour before the arc was finally extinguished. This green-coloured radiation from the sodium arc has been observed by Rayleigh *, but in his experiments it appeared at some distance from the arc. Its production evidently depends upon decreasing vapour pressure, but is difficult to explain on the atomic theory.

As the luminous vapour is distilled from the arc the luminosity persists for a considerable distance along the tube. The subordinate series lines, apparently, all lose intensity in the same ratio, but the D-lines are much less affected, as is shown in spectrogram No. IV. (Pl. XIV.), which was photographed at the window D. By having a small tube F opposite this window the effect of stray light was greatly minimised. This persistence of the D-radiation, as the vapour is distilled from the arc, may be due, partly, to resonance radiation stimulated by light from the arc itself, and incident on the sodium vapour as the latter passes along the tube. Rayleigh † has examined this persistence of radiation for various luminous vapours distilled from the arc.

LXXXV. *The Melting-points of the Normal Saturated Dibasic Acids.* *By* D. A. Fairweather, *B.Sc., Ph.D., Chemistry Department, Edinburgh University* ‡.

THE series of normal saturated dibasic acids has long attracted attention as furnishing a remarkable example of alternation in certain properties between the odd and even members. This effect is most pronounced in the melting-points of the acids : when these are plotted against the number of methylene groups in the chain, two smooth curves are obtained, one for the odd and one for the even members. A similar alternation is observed also in other

* Strutt, 'Nature,' xciii. p. 32 (1914).
† Strutt, Proc. Roy. Soc. A. xc. p. 364 (1914).
‡ Communicated by Professor Sir James Walker, F.R.S.

homologous series, *e.g.* the monobasic fatty acids, whose melting-points rise steadily as the series ascends; the two curves lie close to each other, being separated by only a few degrees. In the series of dibasic acids, however, the odd acids lie upon an ascending curve, whereas the even ones lie upon a descending curve, *i.e.* the even acids have the unique property of continually decreasing melting-point with increasing molecular weight.

It has not hitherto been possible to determine with certainty whether or not the two curves cut each other, as the highest member of the even series previously available was hexadecanedicarboxylic acid, $HOOC.(CH_2)_{16}.COOH$, and many of the melting-points were not determined with sufficient accuracy*. Four new acids higher in the series have now been prepared by Crum Brown and Walker's electrosynthetic method, namely those with twenty, twenty-four, twenty-eight, and thirty-two methylene groups †.

Following is a list of the melting-points of the even dibasic acids, $(CH_2)_n.(COOH)_2$.

	n.	m.pt.
Succinic.....	2	185°
Adipic	4	153°
Suberic	6	140°
Sebacic	8	133°
Decane-dicarboxylic ...	10	129° (127°)
Dodecane-dicarboxylic ...	12	126·5° (123°)
Tetradecane-dicarboxylic ...	14	125° (124°)
Hexadecane-dicarboxylic	16	124° (118°)
Eicosane-dicarboxylic.....	20	123·75°
Tetracosane-dicarboxylic	24	123·5°
Octacosane-dicarboxylic	28	123·25°
Dotriacontane-dicarboxylic	32	123°

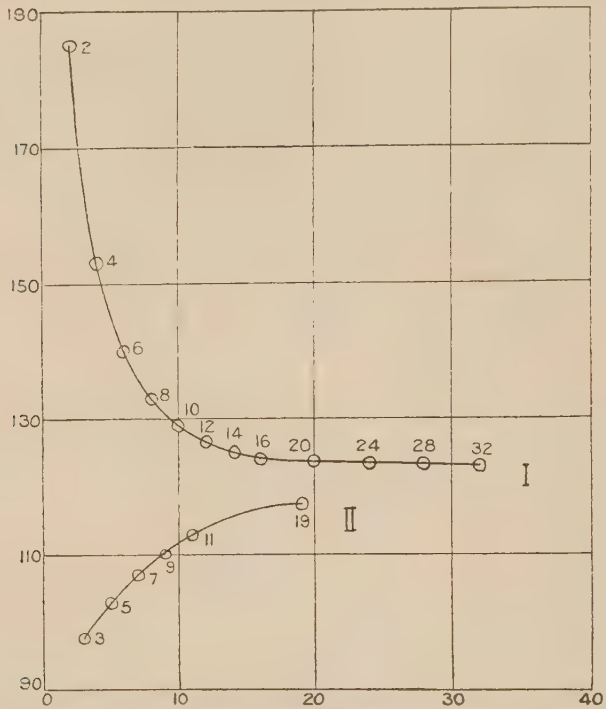
With the exception of the first four, whose melting-points may be taken as sufficiently well established, all these acids were prepared by the author in a specially pure state. The figures in brackets are the melting-points formerly attributed to these acids. In all cases the acids were purified by recrystallization from suitable solvents (chloroform or ethyl acetate) until no further rise in melting-point was observed. A standardized thermometer was used, and a correction for emergent stem applied, giving an error of less than ·25°.

* *Cf.* Cuy, Journ. Am. Chem. Soc. 1920, p. 507.

† Fairweather, Proc. Roy. Soc. Edin. xlv. p. 283 (1925); xlvi. p. 71 (1926).

In the diagram (fig. 1) the melting-points have been plotted against the number of methylene groups in the chain (I.). The corresponding curve for the odd series is also given (II.). The remarkable way in which curve I. flattens out after the point $n=16$ has been reached is at once noticeable; there is, indeed, a difference of only one degree in melting-point due to the subsequent doubling of the hydrocarbon chain.

Fig. 1.



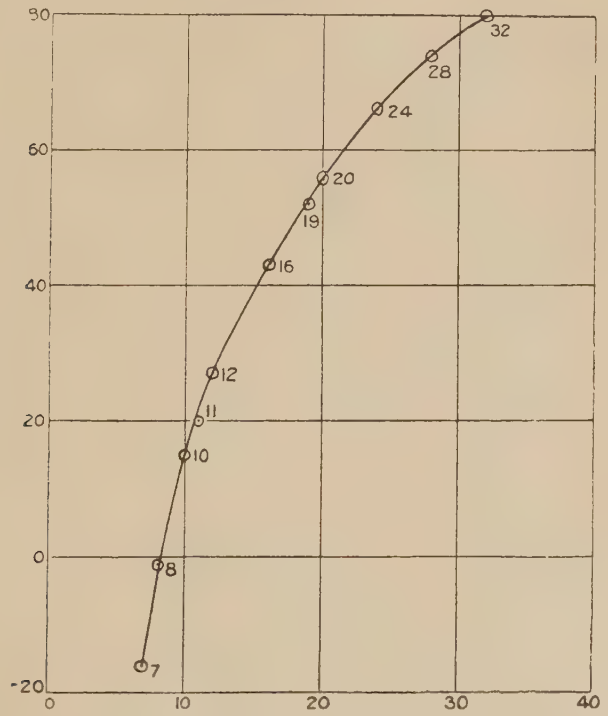
Melting-points of the dibasic acids:—I. even; II. odd. Vertical—m.pt. in degrees Centigrade; horizontal—no. of CH_2- groups. The figures on the curve denote the no. of CH_2- groups.

It has been observed that the most pronounced cases of alternation in homologous series occur (1) where there is a terminal polar group such as carboxyl, and (2) in properties involving the substances in the crystalline state, such as melting-points, heats of crystallization, solubilities, and molecular volumes *. It is therefore probable that the explanation of such alternation is to be found in the crystal structure of the substances.

* Garner & Ryder, Journ. Chem. Soc. 1925, p. 720. Garner & Randall, Journ. Chem. Soc. 1924, p. 881.

In the di-esters of the dibasic acids there is no terminal polar group, and the melting-points show no alternation whatever : they rise in quite a normal manner as the series is ascended, odd and even members alike lying on the same smooth curve (fig. 2).

Fig. 2.



Melting-points of ethyl esters of the dibasic acids. Vertical—m.pt. in degrees Centigrade; horizontal—no. of CH_2- groups. The figures on the curve denote the no. of CH_2- groups.

Following is a list of the melting-points of the diethyl esters of the dibasic acids, $(CH_2)_n \cdot (COOEt)_2$.

Esters.	*n*.	m.pt.	Esters.	*n*.	m.pt.
Azelaic	7	−16°	Nonadecane-dicarboxylic	19	52°
Sebacic	8	− 1°	Eicosane-dicarboxylic	20	56°
Decane-dicarboxylic	10	15°	Tetracosane-dicarboxylic	24	66°
Undecane-dicarboxylic	11	20°	Octacosane-dicarboxylic	28	74°
Dodecane-dicarboxylic	12	27°	Dotriacontane-dicarboxylic	32	80°
Hexadecane-dicarboxylic	16	43°			

The melting-point given in the literature for diethyl sebacate (−4·5°) dated from 1876 *, and it was therefore thought advisable to verify it; no figure was available for diethyl azelate. Specimens of these two esters were accordingly prepared from the pure acids, and fractionated under reduced pressure. They were found to melt at −1° and −16° respectively. The esters of decane- and undecanedicarboxylic acids were similarly prepared and purified. The esters of eicosane-, tetracosane-, and octacosanedicarboxylic acids were purified by recrystallization from petroleum ether, and that of dotriacontanedicarboxylic acid from ether.

In order to explain the fact that malonic and glutaric acids give addition compounds with transchlorodiethylenediamine cobaltic chloride whereas oxalic, succinic, and adipic acids do not, Price and Brazier † have advanced the theory that the odd and even acids have different stereochemical structure, assigning the cis configuration to the odd acids and the trans to the even. Theories of this or similar nature, while perhaps offering an explanation of the existence of separate melting-point curves for the odd and even acids, by no means account for the lowering of melting-point with increase in molecular weight in the even series. We are led, in fact, to look for some peculiarity in the even series itself which does not exist in the odd or in any other known series.

The melting-point of a crystalline solid may be regarded as being largely determined by the magnitude of the forces of cohesion within the crystal ‡. It has been shown that long chain compounds (hydrocarbons, fatty acids, and their esters etc.) have a tendency to arrange themselves side by side as in the monomolecular films obtained by Langmuir and by Adam, especially when pressed flat, the solid substance consisting of a large number of such layers superimposed upon one another §. The flakiness and greasiness of such compounds has been accounted for on this basis as being due to these layers slipping over one another ‖. Each layer of a compound having no terminal polar group has been found to be one molecule thick, but in the case of the fatty acids it is two molecules thick, the carboxyls being attracted to one another and lying in juxtaposition.

* Neilson, Journ. Chem. Soc. 1876, p. 318.
† Journ. Chem. Soc. 1915, p. 1719.
‡ Bragg, 'X-rays and Crystal Structure,' 4th ed. p. 191.
§ Muller & Shearer, Journ. Chem. Soc. 1923, p. 3156. Muller & Saville, Journ. Chem. Soc. 1925, p. 599.
‖ Bragg, 'Concerning the Nature of Things,' 1925, p. 196.

The half esters of the higher dibasic acids (*e. g.* ethyl hexadecanedicarboxylate, $EtOOC.(CH_2)_{16}.COOH$) closely resemble the fatty acids (*e. g.* stearic acid) in their flakiness and greasiness, the two substances instanced being indistinguishable in these respects. The higher dibasic acids themselves, however, do not exhibit these properties in spite of their long hydrocarbon chains, but, on the contrary, are quite hard and brittle. Moreover, there is no reason to suppose that their chains are in any way different with respect to spatial arrangement from those of other chain compounds. This would seem to indicate that each is attached firmly at either end to the carboxyls of its neighbouring molecules. The major forces of cohesion which influence the melting-point would thus be those between the carboxyl groups.

The phenomenon under discussion would appear to be conditioned (1) by the presence of terminal carboxyl groups and (2) by the presence of a chain containing an even number of carbon atoms between them, and may be explained by assuming that the carboxyl groups exert some influence upon each other through the intervening chain. The nature of this influence, moreover, must be such that its transmission through an odd number of carbon atoms entirely alters its character.

As has been pointed out by Challenor and Thorpe *, who were seeking an explanation of the greater chemical reactivity of the odd dibasic acids, the even acids have crossed polarities, *i. e.* the alternate positive and negative charges induced from the carboxyls at either end on each carbon atom of the chain tend to neutralize each other, whereas in the odd series they tend to reinforce each other. In the odd series, therefore, the mutual attraction of the carboxyl groups may be diminished by the presence of like charges upon them, in which case their melting-points would be lower than those in the even series. On this assumption the decrease in melting-point as the even series is ascended may be explained by the fact that as the chain is lengthened, the transmission of the alternate polarity effect is progressively weakened, and the terminal carboxyl carbons become gradually free from the influence of the carboxyl group at the other end of the chain. If this view were correct, it would be expected that when the chain became very long there would be little or no difference between the melting-points of consecutive odd and even acids. That this is indeed the case is very strikingly demonstrated in fig. 1,

* Journ. Chem. Soc. 1923, p. 2482.

in which the two curves appear to approach each other asymptotically.

It has not so far been proved that the alternate polarity effect persists over a number of carbon atoms in a chain united by single bonds, but it is possible that cohesional forces in the crystals as measured by the melting-points constitute a more delicate means of detection of such an effect than has hitherto been used.

LXXXVI. *Investigation of the Zirconium in Colorado Pitchblende.* *By* Oliver Free, *B.A.**

[Plate XV.]

THE study of this mineral was undertaken, since it is peculiar in being the only important uranium mineral stated to contain zirconium and because among the U.S.A. uraninites it is unique in being analogous to the Joachimsthal Pitchblende.

Following an extensive investigation of minerals containing uranium, W. F. Hillebrand (Am. J. Sci. xl. p. 384, 1890; xlii. p. 390, 1891; Bull. U.S. Geological Survey, lxxviii. p. 43) came to the conclusion that uraninites may be divided into two classes, primary and secondary, the first characterized by the presence of thorium and rare earths, the other by their absence. With the former group helium appears to be invariably associated, while in the latter it is present, if at all, only in minute quantities. Besides the chemical differences there is one of another kind, for probably all members of the first group occur in more or less well defined crystals, while those of the second group are generally, if not altogether, massive and free from crystalline form.

Hillebrand found that the Colorado variety occupied a somewhat anomalous position as regards the two groups. Its mode of occurrence and amorphous form, as well as the small percentage of helium, would point to its being a member of the second group, although it may be considered a member of the first group with zirconium in place of thorium and rare earths.

The identity of the constitutent with zirconium was left by Hillebrand in some doubt, and the only test he recorded was that of turmeric paper, which produces a reddish-brown

* Communicated by Professor F. Soddy.

colour when dried after being dipped in a hydrochloric acid solution of zirconium.

The primary uraninites of U.S.A. and Norway all contain a high percentage of lead, corresponding to the high percentage of helium. B. B. Boltwood (Am. J. Sci. xxiii. p. 85, 1907) showed how the age of radioactive minerals could be calculated from the lead-uranium ratio or from the helium-uranium ratio. The former gives a maximum age, while the latter gives a minimum. Boltwood did not take into consideration the fact that thorium as well as uranium produces lead and helium, although not at the same rate, so a new factor has now to be introduced. The conclusion remains unchanged if we consider a uranium mineral that does not contain thorium, as the Colorado Pitchblende.

Besides the anomalous position occupied by the Colorado Pitchblende with respect to the two classes of uraninites, it is interesting in the light of the discovery of hafnium, which resembles zirconium to a very marked degree, and makes it interesting to ascertain whether the element thought by Hillebrand to be zirconium was really zirconium or hafnium.

G. v. Hevesy and T. V. Jantzen (J. C. S. 123, p. 3221, 1923) state that it is well known, chiefly as a result of the measurements made by R. J. Strutt, that all zircons exhibit radioactive properties, by virtue of the presence in them of minute amounts of uranium or thorium. Zircons with large uranium or thorium contents were found to contain rather large amounts of hafnium, and the radioactivity of zircons accordingly show a rough parallelism with the hafnium content.

Since the Colorado Pitchblende contains zirconium in the presence of such a high percentage of uranium, it is therefore of interest to examine the zirconium for hafnium. The optical spectrum of hafnium has been carefully measured by H. M. Hansen and S. Werner (*Kgl. Danske Vid. Selskab Math.-fysiske Medd.* v. p. 8, 1923). The question may be settled either by means of the above optical spectrum lines or by density determinations. In a more recent paper G. v. Hevesy and V. Berglund (J. C. S. 125, p. 2372, 1924) give a density method for determining the ratio of zirconium to hafnium, using the density of their dioxides.

After a careful analytical study of the mineral with particular reference to the elements lead, uranium, thorium, rare earths, and zirconium, sufficient of the mineral was worked up for the zirconia for the density and the spectrum

to be determined. The uranium content was checked by radium estimations by the γ-ray and emanation methods. In addition to uranium as the main constituent, it contained water, silica, zirconia, iron, and a trace of lead, which were estimated. Traces of bismuth, tin, titanium, and vanadium were detected. Aluminium, thorium, and the rare earths were not found.

Analysis of the Mineral.

The specimen of Colorado Pitchblende examined was a single large block obtained from the Colorado-Gilpin, Gold and Radium Mining Company. A microscopic examination only showed the amorphous state of the mineral and the presence of an impurity of iron pyrites, which is shown by its cubic form with striations parallel to two of the edges.

The finely ground pitchblende was dissolved in strong nitric acid (1·42), the action being completed by warming. After dilution the insoluble residue was filtered off and freed from uranium by washing, finally ignited and weighed. The filtrate was then evaporated down to dryness with hydrochloric acid on a sand-bath. Part was rendered insoluble in dilute hydrochloric acid and this part, at first, was mistaken for soluble silica, but later was found to be mainly zirconia.

From the solution Group II. metals were separated with hydrogen sulphide. In minerals containing thorium and rare earths these are next removed by means of oxalic acid in a faintly acid solution. As all tests failed to detect either thorium or rare earths, this step was subsequently omitted.

The uranium was separated by pouring the solution into N/2 ammonium carbonate solution, and estimated chemically by the phosphate method of H. Brearley ('The Analytical Chemistry of Uranium,' 1903).

Lead Determination.

The proportion of lead is important as fixing the maximum age of the mineral and whether it is of primary or secondary origin. The amount of lead formed in one year from one gram of uranium is $1{\cdot}48 \times 10^{-10}$ gram. The age of the mineral is therefore given by $6{\cdot}75 \times 10^{9}$ Pb/U, where Pb/U is the ratio of the amount of lead to the amount of uranium in the mineral. The age of the Colorado Pitchblende as determined from the lead and the uranium contents as obtained by Hillebrand is approximately a hundred million years.

The Group II. sulphide precipitate was very small indeed, and a careful analysis of it showed it to contain principally lead with traces of bismuth and tin. For the estimation of the lead larger quantities of the order of 7·0 grams were used. The method used was to dissolve the well-washed sulphides in dilute nitric acid, add about 5 c.c. of dilute sulphuric acid and evaporate until white fumes are given off freely. After cooling, the residue is treated with 25 c.c. of water and 50 c.c. of alcohol, allowed to stand for some hours and filtered off through a Gooch crucible, which had been dried at a dull red heat inside a nickel crucible. The precipitate was washed free from sulphuric acid with alcohol and dried at a dull red heat as before. The mean of results gave $0{\cdot}0157 \pm 0{\cdot}0017$ per cent. of lead. This gave the age of the mineral of the order of two million years.

It is interesting to compare this age with those obtained by Boltwood for the crystalline U.S.A. uraninites :—

Glastonbury, Conn. ...	410	million years.
Branchville, Conn. ...	530	,, ,,
North Carolina	510	,, ,,
South Carolina	460	,, ,,
Texas	1800	,, ,,

This result therefore proves that the mineral is of recent formation.

Separation and Estimation of Zirconium.

If zirconium was present in the mineral it would be precipitated with iron, etc., as a phosphate during the separation of uranium by the N/2 ammonium carbonate. Zirconium phosphate is very insoluble in acids, even more so than thorium, and the method of analysis makes use of this.

The separation of zirconium from iron, aluminium, and chromium was investigated by P. Nicolardot and A. Reglade (*Compt. Rend.* t. clxviii. p. 348, 1919). The method they employed was to separate as phosphate in a sulphuric acid solution. A 20 per cent. sulphuric acid solution was found necessary to retain all the iron in solution, but at the same time a little zirconium—less than 1 per cent.— was retained in solution.

The best method of precipitation was found to be from a hot dilute zirconium solution in 20 per cent. sulphuric acid by a hot solution of ammonium phosphate containing 10–100-fold excess, finally washing with a 5 per cent. ammonium nitrate solution.

The mixed phosphates were got into solution by fusion with sodium hydroxide and sodium peroxide (3 to 1) in a nickel crucible. After 30 to 40 minutes the melt was cooled and extracted with water. The insoluble residue, consisting principally of sodium zirconate and ferric hydroxide, was filtered off and well washed.

This method of fusion has the advantage not only of the use of a moderately low temperature, but it also makes a partial separation, for those amphoteric elements like aluminium pass into solution and are filtered off. Thus vanadium goes into solution as sodium vanadate and is thereby separated from titanium, which remains behind as sodium titanate. It is therefore possible to distinguish to which element the yellow coloration produced by hydrogen peroxide, in an acid solution, is due. It was noted that, after using a nickel crucible for two fusions, the zirconium became contaminated with nickel.

The residue of sodium zirconate after extraction with water was dissolved in 20 per cent. sulphuric acid to remove the iron. Heating facilitates the solution. Before adding the ammonium phosphate, a few drops of hydrogen peroxide were added in order to retain the titanium in solution as a pertitanate, which in dilute solutions is characterized by a light yellow colour similar to that produced by vanadium. The ammonium phosphate, equal to approximately $1\frac{1}{2}$ times the weight of the mineral taken, was dissolved in 20 per cent. sulphuric acid before being added to the zirconium-containing solution. After boiling for a short time the precipitate was allowed to settle, then filtered off and washed with a 5 per cent. ammonium nitrate solution, dried, finally igniting and weighing as phosphate. The zirconium present is calculated as the dioxide.

The results of successive analyses were not concordant, and search was made for zirconium in the insoluble residue.

Examination of the Insoluble Residue.

Part of the mineral insoluble in strong nitric acid amounted to some 8·75 per cent. This was treated with hydrofluoric acid, fumed with sulphuric acid, and ignited, and the loss in weight recorded as silica.

The residue left was found to contain zirconium, which was estimated as phosphate as before.

Examination of the "Soluble Silica."

On testing the precipitate, thought to be silica, obtained

by evaporating the acid solution of the mineral to dryness, by means of hydrofluoric acid, as above, only in one or two cases was there any loss in weight, and this was exceedingly small. The residue was found to be mainly zirconia.

The results show that there was 5·25 per cent. of zirconia in the mineral, 3·0 per cent. represents the portion separated from uranium as phosphate, 1·5 per cent. that remaining in the insoluble residue, and 0·75 per cent. that obtained as "soluble silica."

This was checked by another method of determination (U.S.A. Dept. of the Interior, Bureau of Mines, Bulletin 212). The powdered pitchblende instead of being dissolved in nitric acid was subjected to an alkaline fusion with sodium hydroxide and sodium peroxide, and the zirconium determined in the insoluble portion. The sodium zirconate was dissolved in hydrochloric acid, and through the boiling solution, after practically neutralizing with ammonia, was passed sulphur dioxide till saturated. The zirconium was precipitated as the hydroxide, which, after filtering and washing with 5 per cent. ammonium nitrate solution, was ignited and weighed as the dioxide. The mean value gave 5·5 per cent. zirconium dioxide.

Determination of Iron.

The iron was determined in the 20 per cent. sulphuric acid solution, after the precipitation of zirconium, by adding tartaric acid, precipitating as sulphide and weighing as oxide, as described by Treadwell and Hall (Analytical Chemistry, vol. ii.). From the microscopic examination it appeared that the iron was present chiefly as an impurity of iron pyrites, so the iron is calculated as FeS_2.

Vanadium was detected in the filtration obtained after extracting with water the melt from the fusion of the mixed phosphates. Addition of hydrogen peroxide to the acidified solution produced a faint yellow colour, and the same solution when reduced with sulphur dioxide gave the distinctive blue colour of the hypovanadate.

Water Determination.

The water was determined by heating the finely ground pitchblende in an air oven at 110° until a constant weight was obtained.

Uranium Estimation.

The chemical method for determining uranium as phosphate as described by Brearley requires practice, as a considerable loss is experienced during the successive filtration owing to the difficulty of washing the filter free from all traces of uranium. The three final determinations gave the following values: 66·5 per cent., 65·0 per cent., and 66·9 per cent. of uranium element. In the calculation of the percentage of U_3O_8 the middle value was omitted, since the other two agree more closely with the value obtained by the emanation method.

Radioactive Estimation. The γ-Ray Method.

The uranium content of the mineral was compared with that of minerals of known uranium content by the γ-ray method, and correcting for the absorption of the γ rays by the mineral (F. Soddy, 'Chemistry of the Radio Elements,' 1915). These indicated the percentage of uranium as between 61·3 per cent. and 70·08 per cent., but the method was abandoned as not giving sufficiently concordant results.

The Emanation Method.

In preparation for this measurement about 0·2 gram of the Colorado Pitchblende was dissolved in a few c.c. of nitric acid, and amounts corresponding to 2·0 mg. of the original mineral were sealed up for a month and the emanation determined in the usual way by means of an emanation electroscope. The electroscope was standardized by emanation from a known quantity of radium, and a leak of one division per minute corresponded to $32{\cdot}4\times10^{-12}$ gram of radium.

The value first obtained was approximately 60·0 per cent. of uranium element, which was below all the chemically-determined values. It was thought that it was probably due to some of the radium remaining in the insoluble residue. The above experiment was repeated as before, only in this case the insoluble residue was first treated with hydrofluoric acid, fused with fusion mixture, and the melt dissolved in hydrochloric acid and placed in a separate emanation flask. After a month the emanation in the new flasks was measured, and found to correspond to 63·2 per cent. and 3·8 per cent. of uranium element respectively, making a total of 67·0 per cent. of uranium element, in good agreement with the final chemically-determined value.

The probable composition of the Colorado Pitchblende a

given by the mean values of the various analyses is as follows :—

U_3O_8	78·9 per cent.
FeS_2	6·7
SiO_2	5·9
ZrO_2	5·25
H_2O	1·75
Residue	1·2
Traces of other elements	0·2
Total	99·90 per cent.

Preparation of Zirconia in Quantity.

Approximately 45 grams of Colorado Pitchblende were worked up for the separation of zirconium in order that the density determinations and the optical spectrum might be obtained.

Quantities of the order of 6 grams were dissolved in concentrated nitric acid. The solution was then evaporated down to dryness with previous addition of hydrochloric acid. The residue was then treated with dilute hydrochloric acid, and the insoluble part filtered off. The excess of acid was practically neutralized before pouring into the N/2 ammonium carbonate solution.

The zirconium was separated in exactly the same manner as described above. In working with the large quantities of zirconium difficulty was experienced in washing the phosphate free from iron during the filtration. Four successive fusions and precipitations were necessary to free the zirconium from iron.

The zirconium was extracted from the insoluble residue by an alkaline fusion without previously treating with hydrofluoric acid, and was kept separate from the rest.

In addition to the zirconium from the Colorado Pitchblende, two other zirconium preparations were prepared for the purpose of comparison. One preparation being from a blue Natural Zircon (Siam), reputed to be rich in hafnium, the other was a Commercial Hydrated Zirconium Oxide.

Density Determinations.

G. v. Hevesy and V. Berglund (J. C. S. 125, p. 2372, 1924) have found that the density of the mixed oxides of hafnium and zirconium could be regarded as a linear function of the composition, and used this method for

determining the percentage of hafnium present. The density of the pure dioxides of both elements was first determined. The two elements had first to be separated by a fractional crystallization of the double potassium fluoride. The mean values they obtained at 20·0° were ZrO_2, 5·73 ; HfO_2, 9·67. The density of the mixed oxide being known, the percentage of hafnium dioxide was calculated by means of the formula

$$x = \left(\frac{d-5{\cdot}73}{0{\cdot}0394}\right),$$

where d is the density of the mixed oxide at 20·0°.

The method of preparing the oxide after the necessary purification of the zirconium phosphate was to remove the phosphoric acid by means of an additional alkaline fusion, the sodium zirconate was dissolved in dilute sulphuric acid and precipitated as the hydroxide with ammonia, and washing free from sodium with a 5 per cent. ammonium nitrate solution. The hydroxide was then transferred to a platinum dish and dissolved in concentrated sulphuric acid, the excess of the latter was driven off on a sand-bath until dryness was obtained, and the remaining acid was expelled at a dull red heat. The final heating at 1000° was done in an electric furnace. The heating was continued until a constant weight was obtained.

The density of the four oxides was obtained by using a specific gravity bottle of 10 c.c. capacity. The bottle was filled with air-free distilled water in a vacuum desiccator, evacuation being continued until no more bubbles of air arose. The bottle and contents were hung for one and a half hours in a thermostat maintained at 20·0°.

Five determinations of each specimen gave the following values :—

Colorado Pitchblende :	
Portion soluble in HNO_3	5·133
Portion insoluble in HNO_3 ...	5·278
Siamese Zircon	5·165
Commercial Hydrated Oxide	5·152

These values are lower than those given by Hevesy for ZrO_2, but they are probably comparable among themselves as an indication of the hafnium content of the four specimens. They show that it cannot be widely different, and it is most probable that hafnium is there only in very small quantities.

It is hoped to have the above specimens subjected to an X-ray analysis, the results of which will be communicated as soon as possible.

Spectroscopy.

To obtain the photograph of the spectra a Féry spectrograph was used, thereby six spectra can be photographed on one negative. Photographs were taken of the four zirconium spectra together with those of the carbon and iron arcs. The latter was used as a standard for calculating the wave-lengths of the required lines.

The negative was projected and the enlarged image examined. Many lines were seen in the zirconium from the Colorado Pitchblende that were not in the other two spectra. Those regions where lines of interest were located were then printed. The wave-lengths of the various lines were calculated by reference to the iron arc standard. All the zirconium lines as given by Exner and Haschek (*Sitzungsb. kais. Akad. Wiss. Wien*, cvii. Abth. II*a*. p. 825; Wellenlängen Tabellen der Bogensp. der Elemente), and reproduced by W. Marshall Watts ('Index of Spectra,' Appendix T), in these regions, were found in the spectra of the preparations from the Colorado Pitchblende, which thus established the identity of the constituent with zirconium.

From the wave-length of the unknown lines, nickel was suspected as an impurity, and upon comparison with a nickel spectrum this was found to be correct. At the same time it should be pointed out that only the very prominent nickel lines showed, and were strongest in the region between 2350 Å.U. and 2310 Å.U., where some fifteen lines were identified. In Pl. XV. the nickel lines are not sufficiently strong to show. The nickel lines were strongest in the portion of zirconium that was soluble in nitric acid.

In addition a group of lines of wave-length : 2545·3, 2552·5, 2555·9, 2560·4, and 2563·3 Å.U. were observed, and then, on reference to Kayser ('Handbuch der Spectroscopie'), were found to agree with scandium lines. The presence of scandium was confirmed by comparison with the spectrum of a scandium preparation kindly supplied by Professor Morgan. It may be recalled that Sir W. Crookes (Phil. Trans. A, ccix. 1909) found scandium closely associated with zirconium in minerals.

The spectra over the regions examined showed no lines, except those of nickel and scandium, not given in the spectrum of zirconium as recorded by Marshall Watts. Several of these are given by Hansen and Werner as due to hafnium, but it is impossible to say with certainty that the lines were actually those of hafnium, since the observed intensity did not agree with those given by Hansen and Werner, nor was there a constant variation.

Plate XV. shows, from left to right, the spectra: (1) a mixed zirconium and nickel preparation, (2) zirconium from Colorado Pitchblende ("soluble silica"), (3) zirconium from Colorado Pitchblende (part soluble in nitric acid), (4) and (5) short and long exposures of scandium oxide, and (6) the carbon arc alone. The magnification is 12·5 times the original negative. The markings in the left-hand gap indicate the position of the zirconium lines as given by Marshall Watts, those in the right, the scandium lines. The scale is graduated in 0·5 Å.U. per division, and acknowledgment is made to Professor Soddy for permission to make use of his calibrated spectroscope and these hitherto unpublished methods for the identification of the spectrum lines.

Summary.

An examination of the pitchblende from Colorado has been made. The lead-uranium ratio was very small and indicates a maximum age of two million years. This establishes the recent formation of the mineral in contradiction to the other U.S.A. uraninites examined by Hillebrand and Boltwood. The identity of the constitutent thought by Hillebrand to be zirconium has been confirmed, and no thorium or rare earths could be detected in the mineral.

The chemical and radioactive analyses of the mineral gave 78·9 per cent. U_3O_8, 5·25 per cent. ZrO_2, with silica, pyrites, and moisture as the important constituents, and traces of lead, titanium, and vanadium.

A comparison of the density of the zirconia separated from large quantities of the mineral with specimens of zirconia separated from a blue Siamese Zircon, reputed to be rich in hafnium, and with a commercial zirconia preparation, showed that all these specimens were of similar low density and therefore of similar low hafnium content. The spectra of the preparations were also similar, and give no evidence of any differences in hafnium content. In the spectra of the specimens from the pitchblende the scandium lines were very clearly shown.

The author's best thanks are due to Professor F. Soddy for suggesting and directing the above research.

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LXXXVII. *The Scattering of Positive Rays by Hydrogen.*

By G. P. Thomson, *M.A., Fellow of Corpus Christi College, Cambridge, and Professor of Natural Philosophy in the University of Aberdeen* *.

[Plate XVI.]

In an earlier paper † an account was given of measurements made on the scattering of positive rays from hydrogen in hydrogen gas. The results were not such as could be explained on the assumption of the inverse square law of force acting between the protons and electrons. The rays in these first experiments were measured by passing them through a slit of variable width into a Faraday cylinder and observing the rate at which it gained charge. This method is not entirely satisfactory for two reasons ‡.

In the first place, the positive rays are continually gaining and losing their charges during their passage through the scattering gas, and it is not certain that the proportion of charged to uncharged rays is the same in the scattered and unscattered portions of the beam. Indeed, as was pointed out in the above mentioned paper, one would expect the scattering, as observed by this method, of molecular rays, which are probably dissociated in the process, to be about half its true value. Secondly, the electrical method, at least in the form used, is not an accurate way of measuring scattering through angles such that the scattered rays are a very small fraction of the total, and it was not found possible to deduce a collision relation from the data obtained.

For these reasons the earlier experiments were considered as giving only the order of the effect, and it was thought best to make further experiments by another method. That chosen was to compare the blackening caused in a photographic plate by the scattered and unscattered portions of a beam of positive rays which were allowed to strike it.

Apparatus.

After some preliminary experiments with unanalysed rays, the apparatus shown in fig. 1 was adopted. The rays generated in the discharge-tube A, pass through two slits B in the cathode C. The slits were of the types used by Aston, and were ·19 mm. wide and 3 mm. across. The

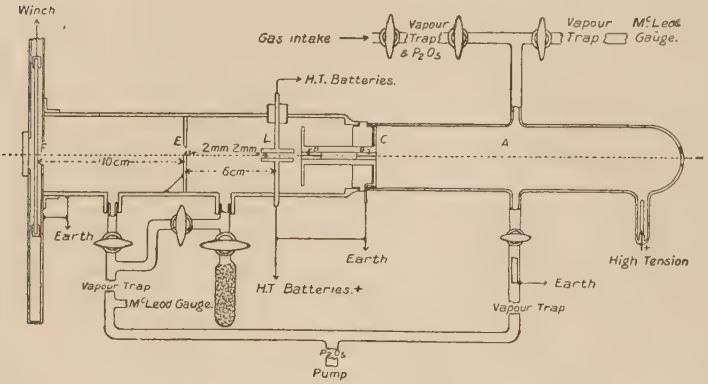
* Communicated by the Author.

† Proc. Roy. Soc. A. cii. p. 197 (1922).

‡ For a correction to the calculations in this paper, see p. 973 (note).

rays then passed between the plates of the condenser L, where they were deflected by an electric field caused by connecting one of the plates of L to the terminal of a battery, the other terminal and plate being earthed. The rays thus spread into an electric spectrum of which a portion was selected by the aluminium slit E, ·5 mm. wide. They then passed through the scattering gas and struck the plate F. This plate could be raised and lowered by means of the usual winch, and several exposures could be taken in rapid succession on the same plate, one above the other.

Fig. 1.



The connexions to gas-holder, pump, and gauges were as shown, and a constant stream of hydrogen, made by the electrolysis of caustic soda and dried with phosphorus pentoxide, was passed through the apparatus. Mercury was carefully excluded by means of traps cooled in liquid air, and the scattering vessel was in connexion with charcoal cooled in liquid air to further purify the hydrogen there.

To obtain the necessary relation between the number of rays and the blackening a series of photographs was taken, each time with varying exposures, the scattering being measured only on the blackest. A typical plate is shown in Pl. XVI.*

As only an electrical separation of the rays was used

* A peculiar effect is shown on practically all the plates. The edges of the strip due to the main beam are appreciably darker than the centre. This is not due to dirt on the slit, which was always very carefully cleaned. It occurs with slits of brass, brass gilded, and aluminium. It is proposed to investigate this effect further.

Note added in Proof.—It now appears that this is an optical delusion of a very persistent type.

these consisted of both atoms and molecules, and it was necessary to allow for this in analysing the results. To do so, an extra exposure was made on each plate (seen at the top in Pl. XVI.) with a magnetic field (not shown in fig. 1) applied just behind E in a direction to give a displacement opposite to that due to L. This will be recognized as a simple form of Aston's mass spectrograph, and gives a line on the plate for each type of ray present. As the pressure in the scattering chamber is high, there is a good deal of "secondary" present seen in the Plate as diffuse illumination, but there was no difficulty in allowing for this in the measurements and determining the proportion of atoms to molecules present. This varied from near equality in one case to cases in which the molecule was so faint in relation to the atom that it could hardly be seen, and measurements were impossible.

Measurements.

The measurements of blackening were made by a selenium cell density meter of the type designed by Messrs. Toy & Rawlings* and made by Watson. This instrument compares densities against those of a standard neutral wedge, and was found very satisfactory.

The following scheme was based on methods used in measurements of the speed of plates. The density of the centre of the pattern was plotted against the logarithm of the exposure time in seconds. This gave a curve, which, in agreement with results obtained for plates acted on by light, showed a straight portion over the region of normal exposure. For very small exposures the blackening was a little more than would be given by producing the straight line, while for over-exposure it grew increasingly less. This curve was then used to translate the measured densities of the scattered rays in the long exposure, into the corresponding intensities of rays. Thus supposing the exposure for scattering was 10 min., and it was found that the blackening at a particular place in the scattered region was the same as that of the centre strip in an exposure of 20 secs., the intensity of the scattered rays is taken as $\frac{20}{600}=3{\cdot}3$ per cent. of the main beam. This assumes, (1) that the intensity of the rays does not alter during the exposure, (2) that the blackening depends only on the total number

* Journal of Scientific Instruments, i. p. 363 (1924).

of rays striking a small portion of the plate, and not on the length of time of the exposure. The first assumption was checked by having the first and last exposure of equal times and rejecting all plates on which their blackening differed to an appreciable extent. The second assumption is rendered probable by the fact that the rays are quite separate entities striking at random. The corresponding law for light has been shown by Schwarzschild not to be strictly true, but even here the divergence is not very great. A similar effect in our case would make a difference to the absolute values obtained for the scattering, but very little to the relative scattering through different angles and for rays of different speed. It should be noticed that the above method of reduction applies equally well even though the centre strip of the exposure measured for scattering is much over-exposed. The measurements were taken only on one side (below) the central strip, this is because the part above is liable to have its blackening increased by rays scattered from the undeviated beam, which of course always exists, and in fact this region is always somewhat blacker than the corresponding point on the other side.

Photographic Effect of the Rays.

The plates used were Paget Process plates, and they were developed for 2 min. at 65° F. in the standard hydroquinone developer recommended by the makers. To secure uniform development the developing tank described by Dobson * was used. The plates were fixed for 1 min. in acid hypo, washed and dried.

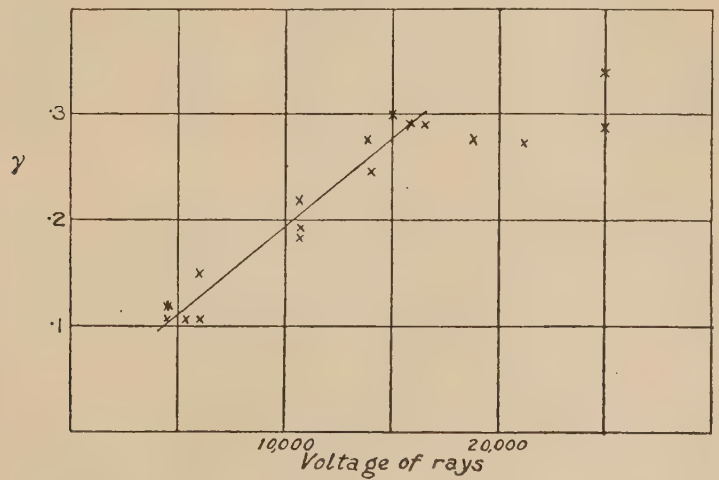
It is of interest to compare the law of blackening of these plates for positive rays with that for light. As mentioned above, the shape of the curve connecting density with the logarithm of the exposure was similar in the two cases. The slope of the straight portion of this curve is the quantity called γ in measurements of the speed of plates. Fabry and Buisson † have developed a theory, which seems to be borne out by experiment, according to which $\gamma = \frac{m'}{m}$, where m is absorption coefficient of the sensitive film for the exciting light, and m' the same quantity for the blackened film, and the light used to measure its density. Thus comparisons of γ under similar conditions of measurement should compare the penetrating power of the rays, and the agreement in the

* 'Nature,' cxiv. p. 752 (1924).

† *Journal de Physique et le Radium*, v. p. 97.

shape of the curve with that found for light suggests that the absorption of the rays like that of light is roughly exponential. Fig. 2 shows γ plotted against the energy of the rays. It will be seen that the relation is a linear one up to an energy of 16,000 volts, after which γ seems to be nearly constant, perhaps owing to the rays going through the whole of the sensitive film. The measurements here, however, are less reliable as the values taken for the exposures did not allow the straight portion of the curve to be drawn with such accuracy as at the lower energies.

Fig. 2.

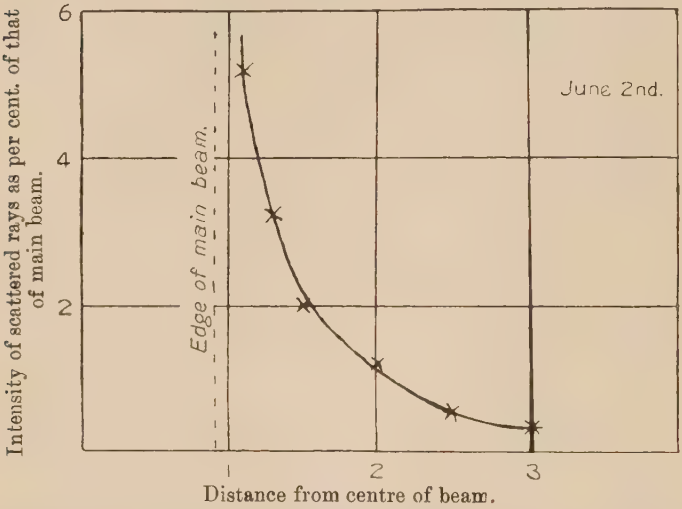


The increase of γ with penetrating power is no doubt the explanation of the results obtained by Aston with Schumanised plates. These plates have the silver bromide concentrated in a very thin layer near the surface, and Aston finds them especially effective for recording the heavier rays. For ordinary plates γ is probably small for these rays owing to their slow speed, which must decrease their penetrating power. Consequently it is almost impossible to get a black negative from them even with prolonged exposure. By using plates with a thin film γ is increased and the conditions are more like those obtaining with hydrogen rays in the ordinary plates. This point is of importance in connexion with the possibility of using methods similar to the above to determine the relative proportions of isotopes, as for such a purpose γ must not be too small.

Reduction of Results.

The measurements obtained give a curve of which fig. 3 is an example connecting the intensity of the scattered rays at a given place with the distance of the place from the centre of the beam of rays. The first stage in the reduction is to deduce from this the corresponding relation which

Fig. 3.



would hold if the beam were an infinitely narrow one instead of being, as it is, of an angle of about 2° giving a width on the plate of 1·8 mm. The beam can be regarded as approximately of uniform intensity over this width, and the following argument then applies. Let $2a$ be the width of the beam at the plate and N the total number of rays per sec. in it. Suppose that a fraction of the rays $f(x)dx$ be scattered through a distance on the plate between x and $x+\delta x$. Then the density of scattered rays at a point ξ from the edge of the main beam is

$$\phi(\xi)=\frac{N}{2a}\int_{\xi}^{\xi+2a} f(x)dx=\frac{N}{2a}\int_{\xi}^{\infty} f(x)dx-\frac{N}{2a}\int_{\xi+2a}^{\infty} f(x)dx.$$

Now in practice $f(x)$ decreases fairly rapidly with x, and it follows that

$$\frac{N}{2a}\int_{\xi}^{\infty} f(x)dx=\phi(\xi)+\phi(\xi+2a)+\phi(\xi+4a)+\ldots\ldots$$

if the series is convergent, as it must be in practice.

Thus the measurements of blackening give the fraction of rays scattered through a distance greater than ξ.

A difficulty arises in applying the above result as the scattering decreases rapidly with increasing distance from the beam, and becomes too small to measure at a distance of a few mm. Thus not more than two terms of the series can be determined experimentally. Though the blackening further out is too small to measure with any accuracy, the corresponding terms in the series may make an appreciable difference to the value of $\int_{\xi}^{\infty} f(x)dx$. The only way of evaluating them is by assuming a mathematical expression for $\phi(\xi)$.

It was shown in the paper referred to above that, assuming the scattering forces followed the inverse square law, $\phi(\xi)$ varies as

$$\frac{1}{\xi^2} - \frac{1}{(2a+\xi)^2}.$$

It was apparent from the first that this was not the case in these experiments. An expression more in accordance with the facts is

$$\phi(\xi) \propto \frac{1}{\xi} - \frac{1}{2a+\xi} \text{ corresponding to } f(2) \propto \frac{1}{x^2},$$

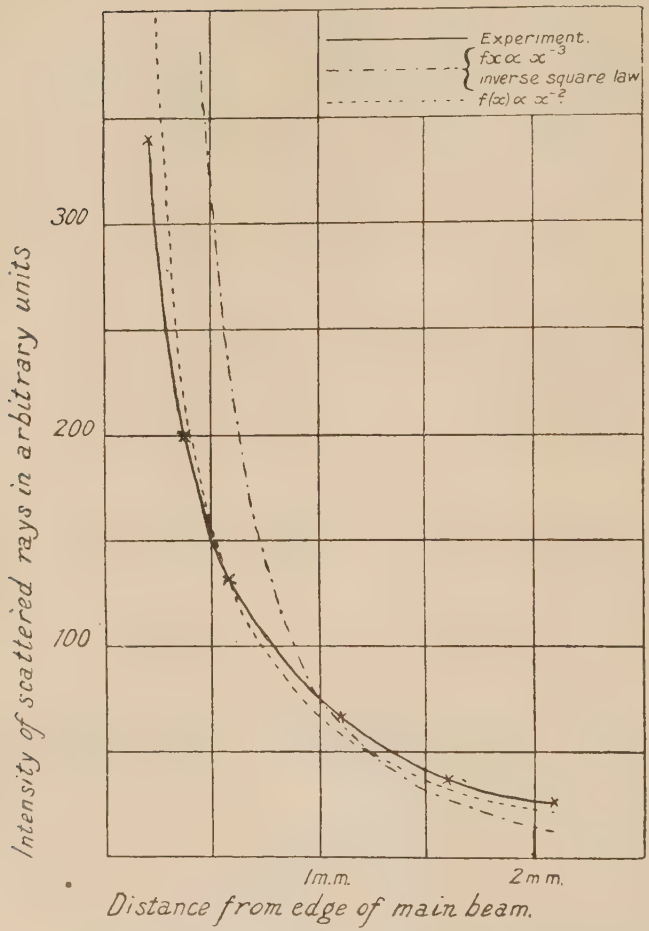
but even this differed from the observations by more than the errors of experiment. If $f(x)$ is taken as varying as a power of x the approximate value of the index is $-1{\cdot}7$. The divergence from the expression

$$\phi(\xi) \propto \frac{1}{\xi} - \frac{1}{2a+\xi}$$

is, however, small except for values of less than ·3 mm. for which the scattering is appreciably less than given by the expression. As will be seen in the next paragraph the scattering very close in may be produced in a different manner, plural scattering, from that further out which is single, and it therefore seems best to neglect the measurements close in ; the rest agree well with the law $f(x) \propto \frac{1}{x^2}$.

The form of the function did not seem to vary with the energy of the rays, and fig. 4 shows the mean value for fourteen experiments compared with two calculated curves.

Fig. 4.



The Nature of the Scattering observed.

A point of fundamental importance in the interpretation of any experiments on scattering is to determine whether the scattering is "single," "plural," or "multiple," *i. e.* whether the bulk of the scattered particles are deflected by only one effective collision, by a small number, or by many. The last possibility can be ruled out for two reasons. It would lead to an error curve for the distribution of the scattered rays which is quite contrary to what is observed, and it is incompatible with the known size of the molecule

as given by kinetic theory arguments. For a pressure of 6/1000 mm., which was not exceeded except for the measurements made to determine the variation with pressure, the total target area per sq. cm. of the hydrogen molecules in the 16 cm. over which scattering took place is 1·28, using Sutherland's value $2{\cdot}17 \times 10^{-8}$ for the diameter of the hydrogen molecule, thus the most probable number of collisions is one.

To distinguish between single and plural scattering is more difficult. Wentzel* has developed an elaborate theory, which, however, requires a knowledge of the collision relation to apply it. As I wish to avoid assumptions as to this at the present stage the following argument is used, which is based only on the observed shape of the scattering curve, and the assumption that the total number of collisions producing detectable scattering is not more than would be deduced from kinetic theory considerations taking the proton as a point. It can easily be shown, assuming the experimental result that $f(x) \propto x^{-2}$, that, if n be the fraction which at one collision is turned through an angle greater than ϵ/l, where l is the length of the scattering chamber, the fraction which is deflected by one collision through a distance on the plate greater than ϵ is $n/2$.

Now choose ϵ so that the fraction observed to be scattered through more than ϵ is 10 per cent. If plural scattering is taking place the number scattered through this distance by one collision only will be less, so we are on the safe side. Now if μ is the chance per unit of path of a deflexion more than ϵ/l, the fraction n making one such collision and one only is $\mu l e^{-\mu l}$. Hence $\mu l e^{-\mu l} > {\cdot}2$. Treating this as an equality we find $\mu l = {\cdot}26$ or $2{\cdot}55$; the latter solution can be neglected from the above kinetic theory considerations, thus $\mu l < {\cdot}26$. The number with two or more such collisions is $1 - e^{-\mu l}(\mu l + 1)$, which is less than ·028 or less than $\frac{1}{7}$ of those with one only. We may neglect this fraction to the order of accuracy of the experiments.

There remains the possibility that there may be enough collisions giving deflexions of less than ϵ/l to produce an appreciable effect. Here we return to the kinetic theory considerations. In the case mentioned before it may be shown that ·35 make one collision only and ·228 make two only, ·138 making more than two. Now if we only consider places outside 2ϵ the first two classes cannot contribute, unless their individual deflexions are each greater than ϵ/l, the case we have already dealt with. Of the remainder

* *Ann. d. Phys.* lxix. p. 335 (1922).

those which make just three collisions are the most numerous and are ·098 of the total. Now 3/4 of these will have two deflexions one way and one the other, so that even in the worst possible case in which all had three single deflexions only slightly less than ϵ/l, only ·025 would have a deflexion on the plate of 2ϵ or more, even if all three collisions took place at the beginning of the path where they would give the biggest displacement on the plate. The collisions are really uniformly distributed over the path through the scattering chamber, and considerations similar to those in the case of single scattering show that the number is approximately halved. Thus ·012 is approximately the number which may have more than 2ϵ deflexion due to plural scattering. Now due to single scattering ·1 have deflexions more than ϵ and following the observed law 05 will have more than ·2ϵ. This is four times those due to plural scattering. Thus we have the following conditions to ensure that the scattering shall be predominately single. Take the distance such that 10 per cent. of the rays are scattered beyond it. Then at twice this distance, *i.e.* where the scattering is 5 per cent., the plurally scattered rays are in a minority of at least 1 in 4, and it is easy to see that their proportion rapidly diminishes further out. Beyond this place then, we have effectively single scattering provided the pressure is not greater than 6/1000 mm. In the experiments considered in this paper the above conditions were always satisfied for distances on the plate greater than ·4 mm. and usually for considerably smaller distances.

Variation of Scattering with Pressure.

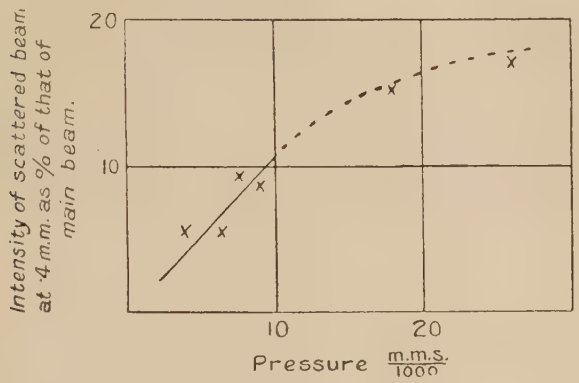
As a check on the above argument a number of experiments were made to determine how the scattering varied with the pressure of the scattering gas. The pressure in the discharge-tube was kept fairly high so that practically all the rays were atomic. The results are shown in fig. 5 plotted against the pressure. The scattering is measured at ·4 mm. from the edge of the main beam. It will be noticed that when the scattering is more than about 10 per cent. it increases much more slowly than in proportion to the pressure, showing that the scattering is becoming plural, as might be expected from the above. The pressures also are higher than 6/1000 mm.

The straightness up to this point suggests indeed that the conditions stated in the last section are unnecessarily severe, which is also borne out by the fact that the shape of the

scattering curve shows no appreciable change for these points.

The scattering at small pressures can be taken from the slope of the straight portion of the curve. The energy of the rays did not vary much in these experiments and averaged 5000 volts.

Fig. 5.



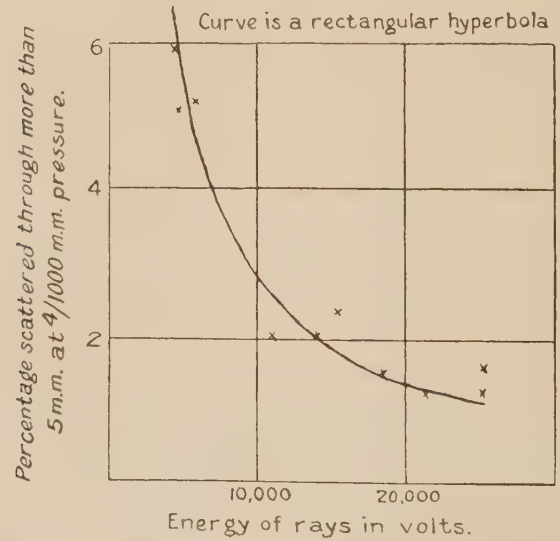
Variation of Scattering with Energy of the Rays.

If the scattering is measured under the conditions of single scattering and reduced to a standard pressure, the way in which it varies with the energy of the ray can be determined. If we may assume that the internal motions of the parts of the molecule are not an important factor, and that the forces are independent of the relative velocity, there is a simple relation connecting the variation of scattering with energy with the function we have called $f(x)$.

In practice the angles through which the rays are scattered are small, and the angular deviation produced in a ray passing through a given field of force is inversely as its energy E. Now suppose the complete expression for the fraction of rays scattered through a distance between x and $x+\delta x$ is ψ (E, x) dx at a small standard pressure. This fraction is the number that pass through a particular portion of the field of force of the scattering molecules, and since the paths of the rays are not appreciably shifted by the small deviations they experience, this number will be the same whatever the energy of the rays. The corresponding deflexions, however, are inversely as E, and it follows that ψ is a function of the product Ex only. Thus, if the variation with x is known, that with E can be deduced.

In the actual experiments care is needed, because in order to obtain rays with large energy the pressure in the discharge-tube has to be kept low, and this results in the production of molecular as well as atomic rays. As mentioned above, the proportion of these was measured. Now the molecular rays will probably show more scattering than the atomic. They have twice as many nuclei to be deflected, and for equal energies of the rays, the nuclei in the molecular ray are moving more slowly and so are more easily deflected. Since, however, a collision violent enough to produce a measurable deflexion would almost always result in a dissociation of the molecule, an uncertainty arises, for we have to compare the photographic effect of part of the dissociated molecule with that of the unaffected ray, and there are not sufficient data to enable this to be done.

Fig. 6.



It seems, however, reasonable to suppose that the scattering of a molecule will be a constant multiple of that of an atom, and if we can choose a reasonable number which will reconcile the results of experiments made with varying energies and varying proportions of atoms to molecules, the result is probably correct. I find that if the molecule is taken as 4 times as much scattered as the atoms, the various points lie approximately on a rectangular hyperbola (fig. 6) in agreement with the form found for $f(x)$. In this

curve the scattering in each experiment is found by finding the value of k which makes $\frac{k}{\xi} - \frac{k}{\xi+2a}$ the best fit to the experimentally observed scattering curve and then taking $k/\cdot 5$ as the measure of the scattering. The process is equivalent to smoothing the curve and correcting for the finite width of the main beam.

Comparison with inverse square law of force.

Although the form of the scattering curve is different from that predicted on the inverse square law, it is of interest to see how the absolute value compares at different parts of the experimental range. In the previous paper the intensity of the scattered rays at a distance y from the centre of a beam of width $2a$ and total strength I was found to be

$$\int_{-a}^{a} \frac{\pi e^2 N l^3}{6\overline{V^2(y-\eta)}^3} \cdot \frac{I}{2a} \cdot d\eta$$

outside a small distance le/Vr from the edge of the beam. To compare with our results as reduced above we want the intensity in the limiting case when a is large, as a fraction of $I/2a$. Performing the integration this is

$$\frac{\pi N e^2 l^3}{12 V^2 \xi^2}, \quad \text{where } \xi = y - a \text{ as before.}$$

Here V is the potential difference through which the rays have fallen to acquire their energy, e is the charge of an electron, N is the number of scattering centres of force, and l is the length of the scattering chamber. In the paper quoted, l was taken as the distance from the diaphragm corresponding to E to the plate. Actually some scattering occurs before the diaphragm is reached, and a more accurate investigation shows that one should write $(l_1^3 - l_2^3)$ for l^3, where l_1 is the distance from the photographic plate to the centre of the condenser, and l_2 is the distance from the latter to the diaphragm *. The number of scattering centres per molecule was taken as two, and if the electrons are free to move this is correct, for the maximum angle of deviation would be 1 in 1850 which is too small to be observed. The possibility of an effect of the electrons is considered below.

* In the previous paper l_1 was 20 cm., l_2 5 cm. $(l_1^3 - l_2^3) = 7{\cdot}875$ against $(l_1 - l_2)^3 = 3{\cdot}375$, thus the calculated scattering as given is too small by a factor of 2·34.

At a pressure of ·004 mm. for rays of 15,000 volts energy scattered through ·5 mm.,

$$\frac{\pi N e^2 (l_1^3 - l_2^3)}{12 V^2 \xi^2}$$

$$= \frac{\pi \cdot 2{\cdot}71 \times 10^{19} \times 2 \times {\cdot}004 \times (4{\cdot}77 \times 10^{-10})^2 \times (16^3 - 6^3)}{760 \times 12 \times 50^2 \times ({\cdot}05)^2}$$

$$= 1{\cdot}05 \text{ per cent.}$$

The observed value from the curve is 1·86 per cent. The table shows the divergence for other conditions within the range of experiment.

Voltage.		% Scattered through ·5 mm.	% Scattered through 2 mm.
5000	Calc.	9·4	1·2
	Obs.	5·6	1·39
15000	Calc.	1·05	·13
	Obs.	1·86	·46
25000	Calc.	·38	·047
	Obs.	1·12	·28

Thus for the slowest rays and small angles the observed scattering is less than that calculated on the simple inverse square hypothesis, while in other cases it is more. The former fact can be explained if it is supposed that the fields of force of the different parts of the molecule partially neutralize one another. It is of interest to consider the distance from the nearest scattering centre at which the rays scattered in various cases will have passed. Owing to the fact that the scattering takes place throughout the volume of the scattering chamber, rays which strike the same portion of the plate will have been scattered through different angles, so that only an average value can be found. Thus take two extreme cases: of the rays of 5000 volts energy 5·6 per cent. are scattered through more than ·5 mm. at 4/1000 mm. pressure, while at the same pressure ·28 per cent. of the rays of 25,000 volts are scattered through more than 2 mm. Now 5·6 per cent. of the rays pass within $2{\cdot}0 \times 10^{-9}$ of one of the nuclei, while ·28 per cent. pass within $·45 \times 10^{-9}$. These distances then give an idea of the regions in which the observed scattering takes place, assuming that the field of force increases in intensity towards the centres in the molecule. Now take Bohr's model of the molecule to give an idea of dimensions, though it is known not to be accurate. The two nearest centres are at a distance of $5{\cdot}84 \times 10^{-9}$. This is about the same as the distance found for the slow rays,

and the defect in scattering in this case may be due to the weak field near the neutral point in the centre of the molecule. This cannot, however, account for the excess of scattering for the faster rays.

It seemed possible that an explanation might be found along the lines that the scattering is not really single, because if the ray comes near one nucleus it has a good chance of being seriously affected by the other. It was found, however, as the result of a somewhat lengthy calculation, that in the case, at least, of the faster rays this effect did not make any appreciable difference to the scattering observed.

The effect of the electrons is difficult to determine, a detailed calculation would involve solving a three body problem, but the following considerations show, I think, that their effect would be small on the classical theory, and probably on the quantum theory also. Since the deflexion due to the free electron is negligible, we shall not be far wrong if we suppose the electron to move so as always to be in a position of equilibrium. But a deflexion such as we have to explain requires an approach to a distance $\cdot 2 \times 10^{-9}$, much smaller than any dimension in the molecule. To hold it in equilibrium one of the nuclei must be at a comparable distance on the other side, and it must be very unlikely that the electron would get forced into such a position by the approach of the ray. On the quantum theory it is of course possible that the stationary orbit behaves like something quite rigid, and it might be possible to explain the observed results on these lines; it seems, however, more in accordance with the general ideas of the theory that the electron should move freely if it gets enough energy to move it to the next orbit, and this would give results of the same order as the classical theory.

It must be remembered that the rays used, though charged at the condenser, pick up an electron in a considerable number of cases in the course of their passage through the scattering gas, and it might be supposed that the neutral atom thus formed undergoes greater scattering. This can hardly be the case, however. For suppose the electron given a sudden sideways velocity by collision with a nucleus or otherwise (though not exactly the truth, this will give the order of the effect). The maximum momentum it can transmit to the ray as a whole will be when it is given just sufficient energy to get clear of the attraction of the proton. If v is the velocity in the orbit this may be changed to $\sqrt{2}v$ in the opposite direction and the whole change of

momentum $(1+\sqrt{2})vm$ transmitted to the nucleus. But the speed of the rays used is not very different from v, so the angle will be about $(1+\sqrt{2})/1850$, which is too small to detect.

Another argument against the electrons being an important factor is the good agreement between the variation of scattering with the speed of the rays observed and what is deduced from the distribution of scattering in a particular case assuming the scattering particles at rest. Owing to the orbital speed of the electrons being comparable with that of the rays, this would not be likely to hold for electron scatttering. Also the shape of the scattering curve is the same for all pressures, while the proportion of neutralized rays increases with the pressure.

It has been shown that the experimental results may be approximately represented by saying that $f(x)$ varies as x^{-2}. It is important to deduce from this the collision relation, *i. e.* the function ψ such that $\psi(\theta)d\theta$ is the chance of a particle after collision making an angle between θ and $\theta+\delta\theta$ with its original direction. To do so account must be taken of the fact that the scattering occurs through a volume and that the scattering measured is the component perpendicular to the slits. In the previous paper the inverse square law, for which $\psi(\theta)$ is proportional to θ^{-3}, was shown to lead to the result that the function we have called $f(x)$ varies as x^{-3}. It can be shown by a similar argument that if $\psi(\theta) \propto \theta^{-2}$ then $f(x) \propto x^{-2}$, the result obtained experimentally. This then is the form of the collision relation. It can be shown that for small angles of scattering, with which alone we are concerned, a centre of force attracting or repelling as the inverse cube will give a collision relation of this form, but it is not legitimate to deduce that such centres really exist because we cannot be certain that the field of force with which we are concerned is radial round one or more centres in the molecule. It might, for example, be concentrated in the neighbourhood of certain lines of force, in which case the above collision relation, or one like it, might occur with quite a different distribution of the field of force.

There is also the possibility that the whole phenomenon is governed by quantum rather than Newtonian mechanics. It is perhaps worth mentioning that the time integral of the *change* in kinetic energy of the ray during its passage through the molecule is of the order of Planck's constant.

Further work is in progress on helium and argon and also to investigate the effect mentioned on p. 962 (note).

Summary.

A method is described of measuring the scattering of positive rays in a gas by measuring the blackening caused by the impact of the scattered rays on a photographic plate.

The density-exposure curve for positive rays is shown to be similar to that for light.

The angles investigated are of the order of $\frac{1}{2}^\circ$ and the scattering is shown to be "single."

The results obtained differ widely from what would be expected on the inverse square law, there being an excess of rays scattered through the larger angles. The variation with the speed of the rays is also different from what would be expected.

The collision relation is found to be of the form $N \propto \theta^{-2} d\theta$, where N is the chance of a particle being scattered between θ and $\theta + \delta\theta$ by one encounter.

This relation is what would result from centres of force acting as the inverse cube.

In conclusion I wish to express my sincere thanks to the Department of Scientific and Industrial Research for a grant towards the expenses of an assistant, and to Mr. C. G. Fraser and the assistant in question, Mr. J. D. McKay, for their very able help in the construction and manipulation of the apparatus used in the above work.

Aberdeen.
Dec. 16, 1925.

LXXXVIII. *The Fine Structure and Zeeman Effect of Complex Mercury Lines.* By Arthur Edward Ruark, *Associate Physicist* *.

Contents.

I. Introduction.
II. Fine Structures of Mercury Lines.
III. Zeeman Effect of Complex Mercury Lines.
IV. Zeeman Effect of Complex Cadmium and Thallium Lines.
V. Conclusion.

I. Introduction.

In a previous paper † it was shown that the fine structures of spectral lines of non-hydrogenic atoms are due to transitions between the components of complex spectral

* Published by permission of the Director of the Bureau of Standards of the U.S. Department of Commerce.

† Ruark & Chenault, Phil. Mag. vol. l. p. 937 (1925). See also Ruark, Mohler & Chenault, 'Nature,' cxiv. p. 575 (1924).

terms. In most cases the complexity of spectral levels is not due to isotopy. Quite frequently complex lines are found in elements which have only a single species of nucleus. Most of the evidence is against the supposition that fine structures are caused by varying orientations of the nucleus (endowed with intrinsic angular momentum) with respect to the electron system of the atom *, though this interpretation may be right in isolated cases. It is believed that small quantized variations in the orbital configurations of loosely bound electrons suffice to explain the existence of most of the fine structures we have studied.

Frequently it occurs that some of the satellites predicted from the energy diagram of the complex levels fail to appear. This makes it probable that integers called *fine quantum numbers* can be assigned to the components of complex levels, and that there are selection principles to govern the changes of these integers when radiation is emitted.

In the paper referred to, no information was given about the fine structure of mercury lines. This element is richer than any other yet studied in the variety and complexity of its fine structures, which are discussed in Section II. of this paper. Section III. deals with the Zeeman effect of complex mercury lines, while Section IV. discusses the Zeeman patterns of complex lines of other elements. Section V. summarizes the results obtained in III. and IV.

The Paschen notation for spectral terms is used because it is found in practically all the sources of the data which are analysed here.

Only those classifications are given which possess a high degree of probability. An enormous amount of experimental work must be done before this subject reaches its final development, and this paper must be regarded simply as a guide for future research. In the present stage of our knowledge it is impossible to assign fine quantum numbers to the complex levels of Hg in an unambiguous manner.

Since the actual wave-numbers of the satellites are of no importance, we shall follow the usual custom of indicating a satellite by giving its distance $d\lambda$ from some arbitrary line of the pattern in thousandths of Ångström units, or the corresponding difference in wave-number, $d\nu$, in thousandths of cm.$^{-1}$. In a few cases it will be necessary to take account of the fact that various authors have used different points of reference in measuring patterns.

* W. Pauli, Jr., *Naturwissenschaften*, xii. p. 741 (1924). See also Ruark, Astrophys. J. lviii. p. 46 (1923).

II. Fine Structures of Mercury Lines.

Most of the mercury lines whose fine structures have been studied have the final orbits $2P$, $2p_1$, $2p_2$, or $2p_3$, so there is a wealth of data available for determining the structure of these levels. On the other hand, we cannot hope at present to obtain much knowledge of the higher lying levels. *E. g.*, the level $4d_2$ is represented only in the line 2652 A., $2p_2$–$4d_2$.

It will be convenient to discuss first the lines which end on $2P$, and then the important triplet $2p$–$2s$, comprising the lines 5461, 4358, and 4047 A. After this we shall take up the other lines in the following order:—

4078 A., $2p_2$–$2S$.

3663 to 2967 A., $2p$–$3d$ and $2p$–$3D$.

2652 A., $2p_2$–$4d_2$, and 2534 A., $2p_3$–$4d_3$.

3341, 2893, and 2752 A., $2p$–$3s$.

2925 A., $2p_1$–$4s$.

2536 A., $1S$–$2p_2$.

The data of Nagaoka, Sugiura, and Mishima* cover a wider range than those of any other author, and have been used, except where otherwise noted, in the hope that a higher degree of internal consistency might be obtained. Professor J. A. Anderson very kindly sent me some unpublished measurements of the lines 5461, 4358, 4047, 3663·28, 3663·05, 3654, 3650, 5790, 5789, and 5769 A. These were made from plates obtained by Drs. Anderson and Mackenzie at Johns Hopkins, in the fifth, sixth, and seventh orders of a 96,000-line grating. Allowing for the fact that the origin of measurement are sometimes different, these excellent data are found to be substantially in agreement with those of Nagaoka, Sugiura, and Mishima. It may be said that the patterns of many mercury lines have been definitely ascertained within the limits imposed by variations in the physical condition of the source; for others, the data of various observers are in conflict and further studies are needed.

Lines Involving the Level 2P.

The patterns given in Table I. yield considerable information about the structure of the level $2P$. The numbers for 5790 A. are from the grating measurements of Gale and

* Japanese Journal of Physics, ii. p. 121 (1923).

TABLE I

Fine Structures of Lines Involving the Level $2P$.

5790·66 A., $2P$–$3D$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−188	1	+561	
−121*	4	+361	g–a
− 78	1	+233	f–a
− 34	2	+101	e–a
0	10	0	d–a
+ 82	1	−245	c–a
+131*	3	−391	
+168	1	−502	b–a
+227*	3	−678	a–a

4347·60 A., $2P$–$4D$.

$d\lambda$.	Int.	$d\nu$.	Classification.
0	2	0	d–a
+ 47	10	−249	c–a
+ 97	3	−514	b–a
+127	3	−672	a–a

5769·60 A., $2P$–$3d_2$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−112	2	+337	
− 50*	4	+150	
0	10	0	g–a
+ 44*	5	−132	f–a
+ 86	1	−258	e–a
+120	1	−361	d–a

5789·69 A., $2P$–$3d_3$.

Author.	$d\lambda$.	$d\nu$.
Gale and Lemon	− 67	+201
	0	0
Wood	− 63	+189
	0	0
Nagaoka and Takamine	− 61	+183
	0	0
Anderson	−120	+360
	− 55	+165
	0	0

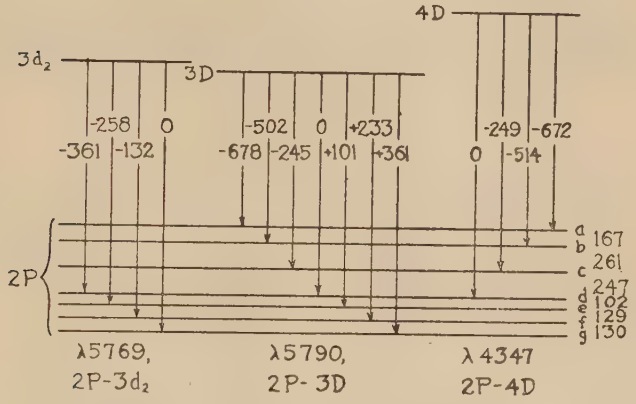
Mean of 201, 189, 183, and 165 is 184.

Lemon *. For 5789 A. we record the data of four observers, together with the mean. The values for 5769 A. represent the mean of several sets of data, all of which are in good agreement. However, Wood † and Nagaoka and Takamine ‡ question the existence of the components at −258 and −361. Lunelund §, Gehrcke and von Baeyer, von Baeyer, Janicki, and Nagaoka all give measurements in close agreement with the pattern recorded for 4347 A.

* Astrophys. J. xxxi. p. 78 (1910).
† Phil. Mag. xxv. p. 443 (1913).
‡ Proc. Phys. Soc. London, xxv. p. 1 (1912).
§ *Ann. d. Physik*, xxxiv. p. 505 (1911). Lunelund gives the complete bibliography.

The similarity of $2P$–$3D$ and $2P$–$4D$ shows that the differences 247, 261, and 167 arise in the level $2P$. The patterns of $2P$–$3D$ and $2P$–$3d_2$ exhibit the successive mean differences 130, 129, and 102, which therefore belong to $2P$. Fig. 1 shows that most of the satellites of these

Fig. 1.



Structures of Lines ending on the Level $2P$.

lines can be classified by the use of these differences. The difference 195 in Anderson's data for $2P$–$3d_3$ is due to $3d_3$. (See the discussion of the lines $2p$–$3d$.) 4344 A., $2P$–$4d_3$, is simple according to von Baeyer (*loc. cit.*), while 4339 A., $2P$–$4d_2$, was measured as a triplet by Janicki, and as a doublet by Nagaoka. The data will not be given here.

4916 A., $2P$–$3S$, is known to be single.

3983 A., $2P$–5F, was measured by Wendt*.

This line has a very broad pattern, symmetrical both in spacing and intensity. The intervals of the eight components are

537×10^{-3} cm.$^{-1}$
366
490
479
477
363
536

Wendt likewise found coarse patterns for 4078 A., $2p_2$–$2S$, and 3341 A., $2p_1$–$3s$. While some of the intervals found by

* *Ann. d. Phys.* xxxvii. p. 535 (1912).

Nagaoka in his study of the last two lines are also represented in Wendt's results, these patterns differ so much from those of other lines that it is probable they have their origin in a physical cause different from that which gives rise to most of the mercury fine structures. For instance, they may be due to the formation of loosely bound Hg_2 molecules. Without a closer description of the Hg-lamp used by Wendt it would be difficult to say whether the pressure was sufficiently high to justify this view. Lunelund * studied the Zeeman effect of 5790 A. and of 5769 A.

TABLE II.

Structure of the Lines $2p$–$2s$.

5461 A., $2p_1$–$2s$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−237	6	+793	c–a
102	3	341	c–b
70	6	234	
47	1·5	157	
19·9	9	66	c–c
8·4	8	27	a–a
0	10	0	b–b
+ 8·2	9	− 29	
18·4	8	62	
85	7	285	b–c
128	3	431	a–b
214	1	717	a–c

4047 A., $2p_3$–$2S$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−116·0	3	+708	c–a
61·4	9	375	b–a
47·5	5	290	
12·3	9	75	
3·9	9	24	a–a
0	10	0	
+ 4·1	9	− 25	c–c
59·2	5	361	b–c
117·0	5	714	a–c

4358 A., $2p_2$–$2S$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−238	1	+1258	
206	1	1082	
160	7	844	c–a
108	7	566	
95	4	502	b–a
47	1	245	
21	8	110	c–c
9	8	47	b–b
3	10	15	
+ 3	10	15	
19	5	99	a–a
29	3	154	
46	1·5	244	b–c
108	7	566	a–b
159	3	834	a–c
182	5·5	956	
224	1	1176	
238	1·5	1251	

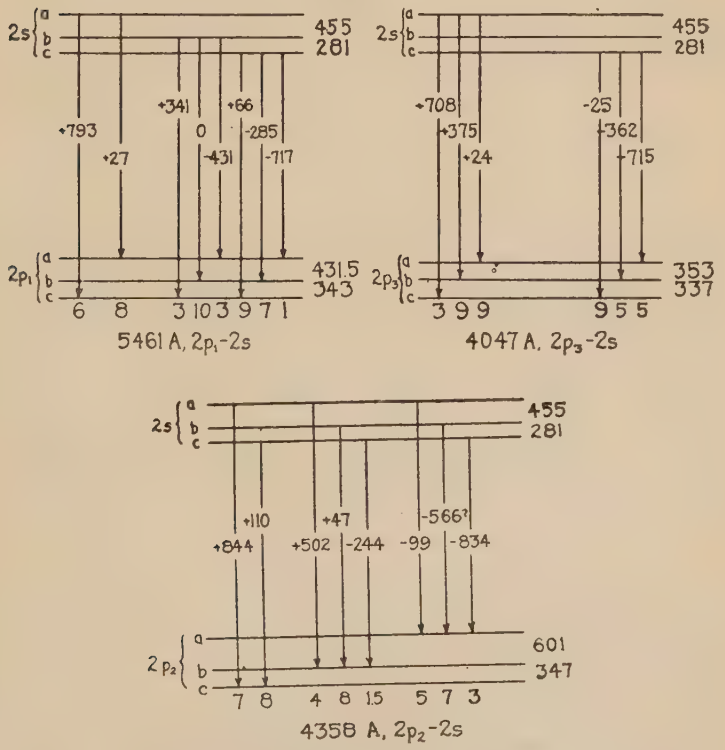
* *Loc. cit.*

in low fields. The satellites which could be definitely traced are marked with asterisks in Table I. All of these exhibited the same separations as the main lines. (5769 was not fully resolved.) Lunelund observed shifts of the parallel components of some satellites, which throw no light, however, on the problem of classification.

5461, 4358, *and* 4047 A., $2p$–$2s$.

The structures of these lines, as shown in Table II. and fig. 2, are based on a sure foundation of experimental fact.

Fig. 2.



Structures of the Sharp Series Triplet $2p$–$2s$.

They have been studied by a large number of observers, and the results of all those who have done considerable work on fine structures are in substantial agreement. The data given

are those of Nagaoka *. The existence of numerous unclassified satellites makes it very probable that there are other components of the level $2s$. The reader may refer to the section on the lines $2p$–$3d$ for information about some doubtful components of the level $2p_1$.

4078 A., $2p_2$–$2S$.

Five authors agree that the pattern of $2p_2$–$2S$ is substantially as given below. The data are those of Nagaoka,

$d\lambda$.	Int.	$d\nu$.	Classification.
−77	4	+464	
−47	5	+283	d–a
0	10	0	c–a
+32	3	−193	
+50	5	−301	
+76	2	−457	

Sugiura, and Mishima †. Wendt ‡ observed a complicated pattern nearly one Angström in width, which has not been found by anyone else. (For further details, see the section on lines which involve the level $2P$.) He also studied the Zeeman effect of this line in strong fields. Most of the satellites disappear or coalesce, and the pattern becomes a 3/2 normal triplet; each of the perpendicular components is accompanied by two satellites, one on either side, at average separations of +192 and −283. There is much evidence that the difference 283 is characteristic of $2p_2$.

3663 *to* 2967 A., $2p$–$3d$ *and* $2p$–$3D$.

The data for this group, summarized in Tables III., IV. V. and figs. 3 and 4, are those of Nagaoka, Sugiura, and Mishima, with the following exceptions. The data for 3663·05 show a considerable variation, and those of Wendt have been adopted for the sole reason that they exhibit differences known to be characteristic of $2p_1$ and of $3d_3$. The satellite $d\nu = +104$ of 3663·28 A. was observed by Anderson only (unpublished), while the value $d\nu = -873$

* Proc. Phys. Soc. London, xxix. p. 91 (1917).
† *Loc. cit.* ‡ *Loc. cit.*

is the mean of measurements made by Wendt and by Takamine.

TABLE III.

Structures of $2p_1$–$3d_{1,2,3}$ and $2p_1$–$3D$.

3663·28 A., $2p_1$–$3D$.

$d\lambda$.	Int.	$d\nu$.	Classification.
− 91·0	2	+678	
50·7	0·5	378	
14	00	104	
0	10	0	m–a
+ 9·4	1	− 70	b–a
15·9	2	118	
32·8	0·2	245	
42·5	0·4	317	
68·1	0·8	508	a–a
117·0	1	873	

3663·05 A., $2p_1$–$3d_3$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−104	1	+775	c–c
77	1	574	
26	1	194	a–b
0	10	0	a–c
+ 53	2	−395	
109	1/2	813	

3654·83 A., $2p_1$–$3d_2$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−97·3	5	+728	
72·4	4	542	
37·3	1·5	279	c–a
29·8	?	223	n–a
21·3	1	160	
7·6	1	57	
0	10	0	m–a
+ 9·5	2	− 71	b–a
33·9	0·5	254	
49·3	1	369	
67·7	6	506	a–a

3650·15 A., $2p_1$–$3d_1$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−54·1	4	+406	
41·7	5	313	
30·1	7	226	n–a
23·9	4	179	
16·8	9	126	
9·0	2	68	
0	10	0	m–a
+10·3	1	− 77	b–a
92·4	7	694	

The patterns of 3663·28, $2p_1$–$3D$; 3654, $2p_1$–$3d_2$; and 3650, $2p_1$–$3d_1$, present certain similarities which lead to the introduction of a pair of doubtful components m and n in the level $2p_1$, as shown in fig. 3. The difference 225 appearing in the data for these lines is encountered also in $2p_1$–$2s$ and $2p_1$–$3s$.

Table IV.

Structures of $2p_2$–$3d_{2,3}$, $2p_2$–$3D$, and $2p_2$–$4d_2$.

3131·84 A., $2p_2$–$3D$.

$d\lambda$.	Int.	dv.	Classification.
−12·8	1	+130	
9·9	5	101	d–a?
5·1	1·5	52	
0	10	0	
+ 5·7	8	− 58	
18·0	0·5	184	c–a?

3131·56 A., $2p_2$–$3d_3$.

$d\lambda$.	Int.	dv.	Classification.
−82·0	4	+836	
54·4	1	554	
23·7	5	242	
13·0	2	133	c–a
8·3	4	85	
4·3	5	44	
0	10	0	d–b
+27·6	5	−282	c–b

3125·66 A., $2p_2$–$3d_2$.

$d\lambda$.	Int.	dv+42.	Classification.
−205·7	2·5	+2148	
100·8	0·3	1074	
76·8	9	818	d–a
48·3	8	537	c–a
35·4	0·5	404	
25·2	2	300	
14·5	1	190	b–a
8·3	4	127	
0	10	42	
+ 12·1	1	− 82	
15·4	0·7	115	
20·2	5	165	
42·1	9	389	
70·6	1	681	

2652·04 A., $2p_2$–$4d_2$.

$d\lambda$.	Int.	dv.
−27·9	2	+397
15·9	1·5	226
5·5	10	78
0	10	0
+ 6·3	1	− 90
11·3	2	161
22·6	4	322
37·5	0·5	534

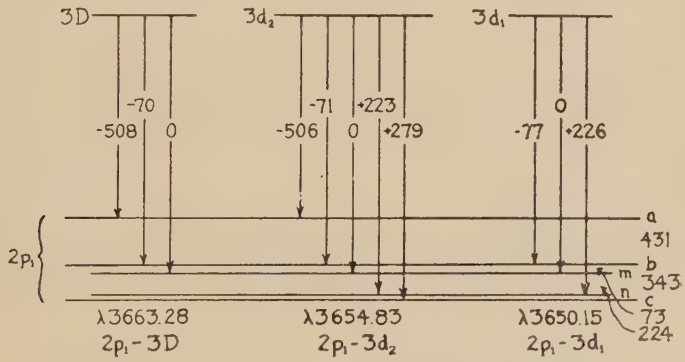
The structure of the lines $2p_{1,2,3}$–$3d_3$ shows that the level $3d_3$ has three components separated by 413 and 195, beginning with the level of smallest wave-number. The difference 608–413=195 occurs also in the pattern $2p_3$–$4d_3$, so that $3d_3$ and $4d_3$ may have structures which are somewhat similar.

TABLE V.

Structures of $2p_3$–$3d_3$ and $2p_3$–$4d_3$.

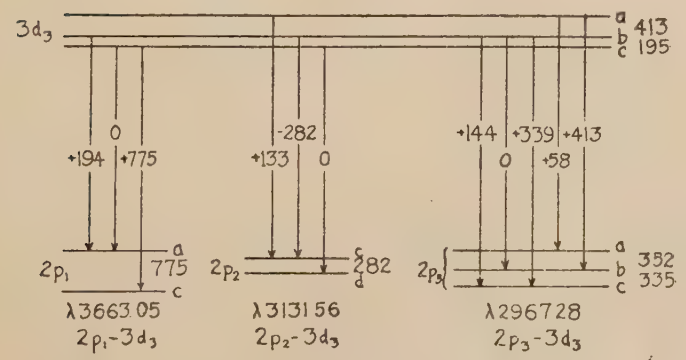
2967·28 A., $2p_3$–$3d_3$.				2534 A., $2p_3$–$4d_3$.			
$d\lambda$.	Int.	$d\nu$.	Classification.	$d\lambda$.	Int.	$d\nu$.	Classification.
−193·8	0·7	+2205		−33·3	6	+518	c–b?
37·9	0·2	431		22·6	7	352	b–a
36·3	8	413	b–a	11·3	9	176	b–b?
29·8	7	339	c–b	0	10	0	a–a
12·7	6	144	c–c	+12·5	5	−195	
5·1	8	58	a–a	24·5	3	389	
0	10	0	b–b				
+ 17·1	3	− 133					

Fig. 3.



Structures of the Lines $2p_1$–$3D$, $2p_1$–$3d_2$, and $2p_1$–$3d_1$.

Fig. 4.



Structures of the Lines $2p_1$–$3d_3$, $2p_2$–$3d_3$, and $2p_3$–$3d_3$.

TABLE VI.

Structures of $2p_{1,2,3}$–$3s$ and $2p_1$–$4s$.

3341·48 A., $2p_1$–$3s$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−222·2	0·5	+1990	c–x?
183·8	1·5	1645	b–x?
91·4	2·5	818	
79·4	2	711	
37·3	0·2	334	
27·0	1·5	242	
18·8	0·5	168	
8·2	8	073	
0	10	0	c–a
+ 25·1	6	− 225	
44·0	0·5	394	
86·6	5	775	a–a
94·8	3	849	
137·1	0·3	1228	
212·2	1	1900	
352·9	4	3160	
400·5	0·1	3588	

2893·60 A., $2p_2$–$3s$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−201·7	2	+2409	
128·9	0·5	1540	
68·5	3	818	d–a
45·0	0·5	538	c–a
37·6	0·5	449	
15·9	0·2	190	b–a
6·3	6	75	
0	10	0	
+ 8·3	1·5	− 99	
13·5	0·7	161	
17·5	3	209	
48·7	1·5	582	
68·8	1	822	
80·3	1·5	960	

2752·78 A., $2p_3$–$3s$.

$d\lambda$.	Int.	$d\nu$.	Classification.
−177·3	0·5	+2341	
121·9	0·5	1610	
61·2	1·2	808	
25·8	3	341	
21·7	1	287	
18·5	0·1	245	
2·8	9	37	
0	10	0	
+ 28·2	1	− 373	c–a
53·7	2	710	b–a
117·0	0·7	1546	
185·5	0·5	2450	
229·5	1	3033	
238·9	0·5	3156	

2925·41 A., $2p_1$–$4s$.

$d\lambda$.	Int.	$d\nu$.
− 69·2	2	+ 809
51·8	1	606
20·9	1	244
0	10	0
+ 22·5	2	263
69·0	1·5	807
137	0·5	1602

In the pattern of 3125 A., $2p_2$–$3d_2$, we find a group, −165, +190, +537, and +818, which is duplicated in 2893 A., $2p_2$–$3s$. The difference 355 between −165 and +190 is not understood, but the other differences involved are easily recognized in other lines ending on $2p_2$.

Wendt * found that 2967·52 A., $2p_2$–$3D$, has one satellite at $d\nu = +704$. Within the error of measurement, this difference is identical with $d\nu = 690$, occurring between the levels a and c of $2p_3$.

Other Lines Involving $2p_1$, $2p_2$, and $2p_3$.

None of the satellites of 2652 A., $2p_2$–$4d_2$, Table IV., have been classified, but it is worth while to notice that the group −161, −90, 0, and 78 is repeated with great exactitude in the pattern of 2893 A., $2p_2$–$3s$.

The data for 2534 A., $2p_3$–$4d_3$, Table V., indicate the existence of a difference 176 in $4d_3$, but there is no independent check.

The broad and complicated patterns of $2p_{1,2,3}$–$3s$, Table VI., show many resemblances; we record only those classifications which seem reasonably certain. It will be seen that the difference 377 is especially prominent, but it is difficult to interpret.

Professor R. W. Wood has kindly placed at my disposal the results of his investigations on the structure of 2536 A., $1S$–$2p_2$. He has shown that many of the components given by Nagaoka, Sugiura, and Mishima are due to self-reversals. The data are given in the table below :—

$d\lambda$.		$d\nu$.	Remarks.
Wood.	Nagaoka et al.		
−14	−14·6	+227	
0	0	0	
+10	+ 9·8	−152	
+21	+20·4	−318	Nagaoka et al. record lines at +21·6 and 19·3, probably due to self-reversal. The mean is listed here.
+31	+31·5	−490	

Particular attention should be directed to the differences 172 and 166 appearing in this pattern. They are probably characteristic of $2p_2$, judging from the frequency with which they occur in other lines involving this level.

* *Loc. cit.*

Summary of the Structures of Complex Mercury Levels.

We give below the differences between the components of complex spectral levels, beginning at the top of the energy diagram.

Energy Level.	$d\nu$ in 10^{-3} cm^{-1}.	Interval.
$4d_3$	176?	ab
$3s$	1990?	xa
$3d_3$	413	ab
	195	bc
$2s$	455	ab
	281	bc
$2P$	167	ab
	261	bc
	247	cd
	102	de
	129	ef
	130	fg
$2p_1$	431·5	ab
	343	bc
	73?	bm
	224?	mn
$2p_2$	601	ab
	347	bc
	282	cd
$2p_3$	353	ab
	337	bc

III. The Zeeman Effect of Complex Mercury Lines.

Nagaoka and Takamine * have studied the Zeeman effect of 5461, 4359, and 4047 A. very thoroughly, from the lowest fields which gave an observable splitting up to 30,000 gauss. The reader should refer to their diagrams of the complicated patterns obtained. Unfortunately, they do not give complete tables of numerical data, so the following discussion depends mainly on values obtained from the diagrams.

In commencing the analysis of these patterns, we first note the existence of the following magnetic levels, expressed in terms of the unit $\Delta\nu_{\text{normal}}$. These levels behave in approximate accordance with the usual laws, the deviations amounting at most to a few per cent.

* Proc. Tokyo Math.-Phys. Society, vii. pp. 188 & 331 (1913), or Phil. Mag. xxvii. p. 333 (1914), and xxix. p. 241 (1915).

Line.	Level. a.	b.	c.
$2s$	+2, 0, −2	+2, 0, −2	+2, 0, −2
$2p_1$	+3/2, 0?	+3, +3/2, 0, −3/2, −3	
$2p_2$	+3/2, 0, −3/2*	+3/2, 0, −3/2	+3/2, 0
$2p_3$	0	0	0

The evidence for these conclusions is drawn from the approximately normal behaviour of certain components of the following satellites :—

Line.	Satellite.	Classification.	Components utilized.
λ 5461	0	b–b	
	− 66	a–b	*s*-component.
	−285	b–c	*p*-branch of longer wave-length.
	−431	a–b	*p*-branch.
λ 4358	+110	c–c	*s*-components.
	− 99	a–a	*s*-components.
	−244	b–c	
	−566	a–b	
λ 4047	+ 24	a–a	
	− 25	c–c	
	+375	b–a	*s*-components.
	−362	b–c	*s*-components.

Consider the satellites +375 of λ4047, b–a, and +793 of λ5461, c–a, which split into two parallel components. The components of shorter wave-length show exactly the same type of separation. It is reasonable to suppose that all the variation is to be ascribed to the magnetic level belonging to "a" of $2s$. This shows that "b" of $2p_3$ has a level with magnetic quantum number 0, which retains its original position. The same is true of "c" of $2p_1$. It is found that the magnetic level belonging to $2s$, a, moves in such a way as to join that level of $2s$, b, which has a magnetic quantum number +1. The change is practically complete at 10,000 gauss. This phenomenon is strikingly similar to the Paschen Back effect.

Further analysis of these patterns would be difficult in the present stage of our knowledge. Most of the remaining

* This value is correct only in weak fields. Separations become greater than ± 3/2 above 2000 gauss.

components have separations which are not proportional to the field and coalescence of components occur in many cases.

Wendt (*loc. cit.*) has examined the Zeeman effect of the lines $2p$–$3d$ and $2p$–$3D$ in strong fields. His observations were made with a grating, and it is probable that the details will be somewhat revised when higher resolving powers are applied to the problem. He found that most of the satellites disappear in comparatively weak fields. Wendt gives no numerical data, but states that the patterns of certain lines are in agreement with the findings of Runge and Paschen. The types observed in other cases may be inferred with reasonable certainty from the drawings given. The results are collected in Table VII., where patterns obtained from the drawings are indicated by asterisks.

TABLE VII.

Zeeman Effects of the Mercury Lines $2p$–$3d$ and $2p$–$3D$.

λ.	Classification.	Observed Zeeman Patterns.	Predicted Zeeman Patterns.	Remarks.
3663·28	$2p_1$–$3D$*	?	$\frac{(1),\ 2,\ 3,\ 4}{2}$	
3663·05	$2p_1$–$3d_3$*	$\frac{(2),\ (4),\ 1,\ 5}{2}$	$\frac{(0),\ (2),\ 1,\ 3,\ 5}{2}$	The interpretation of the observed patterns of 3663·05 and 3654·83 is very doubtful.
3654·83	$2p_1$–$3d_2$*	$\frac{(2),\ (4),\ (6),\ 3,\ 5,\ 7,\ 9}{6}$	$\frac{(2),\ (4),\ 5,\ 7,\ 9,\ 11}{6}$	
3650·15	$2p_1$–$3d_1$	As predicted.	$\frac{(0),\ (1),\ (2),\ 6,\ 7,\ 8,\ 9,\ 10}{6}$	
3131·84	$2p_2$–$3D$*	$\frac{(0),\ (1),\ 2,\ 3}{2}$	$\frac{(0),\ (1),\ 2,\ 3}{2}$	There are also ⊥ components at about $0{\cdot}6\ \Delta\nu_{\text{normal}}$.
3131·56	$2p_2$–$3d_3$*	$\frac{(0),\ (2),\ 1,\ 3}{2}$	$\frac{(2),\ 1,\ 3}{2}$	There are two weak ⊥ components outside the components $\pm 3/2$.
3125·66	$2p_2$–$3d_2$	As predicted.	$\frac{(0),\ (2),\ 5,\ 7,\ 9}{6}$	
2967·52	$2p_3$–$3D$	Normal.	Normal	Satellite at $d\nu = +704$ disappears in strong fields.
2967·28	$2p_3$–$3d_3$	As predicted.	$\frac{(0),\ 3}{6}$	

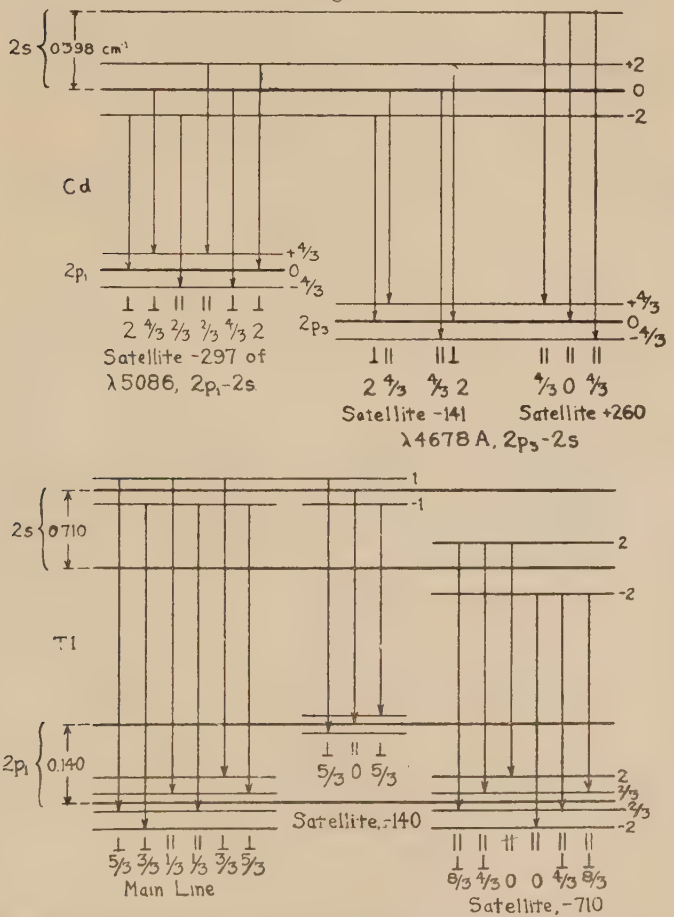
IV. Zeeman Effect of Complex Cadmium and Thallium Lines.

1. *Cadmium.*

Wali-Mohammad* studied the Zeeman effect of the cadmium lines $2p_{1,2,3}$–$2s$ up to fields of about 5000. The principal lines of these patterns have anomalous Zeeman effects of the usual type.

The more refrangible satellite of 5086 A., $2p_1$–$2s$, moves toward the main line; the satellite at $dv = -297$ becomes a

Fig. 5.



Suggested Interpretation of the Zeeman patterns of Complex Cadmium and Thallium Lines.

* *Ann. d. Phys.* xxxix. p. 225 (1912).

sextet which may be interpreted as shown in fig. 5. The behaviour of the satellites of 4800 A., $2p_2$–$2s$, is so complicated that no certain conclusions can be drawn as to the alterations of the spectral levels. The behaviour of the two satelites of 4678 A., $2p_3$–$2s$, is also shown in fig. 5. The satellite at +260 has two perpendicular components at $\pm 1{\cdot}60\ \Delta\nu_{\text{normal}}$, which have not been classified. A new satellite appears at +0·018 A. when the field is applied.

2. *Thallium.*

Back * found that the main line 2767·913 A. of the configuration $2p_2$–$3d_2$ gives approximately the $p_2\,d_2$ pattern,

$$\frac{\pm\,(1),\ 11,\ 13}{15}.$$

The satellite at $d\nu = +404$ has a pattern which agrees well with

$$\frac{\pm\,(1),\ 25}{15},$$

while the pattern

$$\frac{\pm\,(1),\ 11,\ 25}{15}$$

should be obtained if the d_2 level which is involved in producing this line has magnetic components at $\pm\,2/5$ and $\pm\,10/5$ times $\Delta\nu_{\text{normal}}$.

Wali-Mohammad † studied the Zeeman effect of 5350 A., $2p_1$–$2s$. The main line has the Zeeman pattern appropriate to its classification,—that is

$$\frac{\pm\,(1),\ 3,\ 5}{3},$$

while the satellite at $d\nu = -140$ has

$$\frac{\pm\,(0),\ 5}{3},$$

and that at $d\nu = -710$ splits into

$$\frac{\pm\,(0),\ (4),\ (8),\ 4,\ 8}{3}.$$

* *Ann. d. Phys.* lxx. p. 333 (1923).
† *Loc. cit.*

These results can be interpreted as shown in fig. 5. Of course, other arrangements are possible.

V. Conclusions concerning the Zeeman Effect of Complex Lines.

The existing observations on the Zeeman effect of complex lines do not suffice to yield us general rules for the prediction of Zeeman patterns from a knowledge of the quantum numbers of a given level.

However, in all patterns which have been investigated definitively the main line has the Zeeman pattern appropriate to simple lines of the same series notation. In general, the "splitting factors" (the g's of Landé) are the same for subsidiary components of a complex level as for the corresponding simple levels: for example, many of the mercury satellites show the same type of separation as the main lines. Still, there are exceptions which are experimentally well verified. We have seen that Wali-Mohammad found separations of 2 times $\Delta\nu_{\text{normal}}$ for the lower component of the level $2s$ of cadmium, and 4/3 times $\Delta\nu_{\text{normal}}$ for components of $2p_1$ and $2p_3$ of that element. These separations are, respectively, characteristic of $2s$ and $2p_1$ of a doublet system.

Many cases occur in which expected components are lacking, and anomalies of polarization such as unpolarized components are also found. We have seen many instances in which fine structure separations are unaltered by magnetic fields, just as in hydrogenic atoms, and others in which the components coalesce, so that the p pattern in strong fields approaches the anomalous Zeeman effect of a simple line of the same classification. W. Pauli, Jr.*, has pointed out that the latter type of behaviour is to be expected if fine structures are due to varying orientations of a nucleus which possesses an intrinsic angular momentum. Of course, other causes for such a behaviour can readily be suggested.

* *Naturwissenschaften*, xii. p. 741 (1924).

LXXXIX. *Dilatometric Investigation of the* A_3 *and* A_4 *Transformations in Pure Iron.* *By* Seikichi Satô *.

§ I. *Introduction.*

THE magnetic investigation of the A_3 and A_4 transformations in iron has already been made by Curie †, Weiss & Föex ‡, and others §. Among them Prof. T. Ishiwara, from the result of his experiment with a torsion balance, showed that during heating the magnetic susceptibility of pure iron increases discontinuously at the A_4 point and afterwards gradually decreases, and, on cooling, the change is reversed.

From his study of the A_3 and A_4 transformations with regard to the changes in physical properties of pure iron at high temperatures, Prof. K. Honda predicted that by the A_4 transformation γ-iron will be re-transformed to α-iron, that is, δ-iron will be the same as α-iron. A year later this was actually confirmed by Westgren || by X-ray analysis.

The answer to the question, whether during the Ac_4 transformation iron will expand or contract, is not evident; because this depends on the coefficient of expansion of γ-iron. The present investigation was undertaken to decide this point experimentally. Since the A_4 point lies at so high a temperature as 1400°, this investigation is not an easy matter. The writer carried out his investigation with a very pure iron and succeeded in finding a distinct expansion during the Ac_4 transformation. In fact the thermal dilation curve of δ-iron formed the continuation of that of α-iron, showing that the α- and δ-irons are in the same state of aggregation.

§ 2. *Arrangement and Method of Experiment.*

The present experiment was commenced with a dilatometer similar to that used by Prof. K. Honda ¶; the heating wa effected by the carbon ring electric furnace, devised by Rosenhain and subsequently modified by Lecturer S. Kaya **

* Communicated by Prof. K. Honda.

† Curie, Œuvres, p. 289.

‡ Weiss & Föex, *Arch. des Sci. Genève*, xxxi. p. 89 (1911).

§ K. Honda & H. Takagi, Sci. Rep. iv. p. 261 (1915). T. Ishiwara, Sci. Rep. vi. pp. 133–138 (1917). E. M. Terry, Phys. Rev. ix. p. 394 (1917).

|| Westgren, Engineering, p. 631 (1922); *Stålets Kristallbygnad* (1921); Journ. Iron & Steel Inst. i. p. 240 (1922).

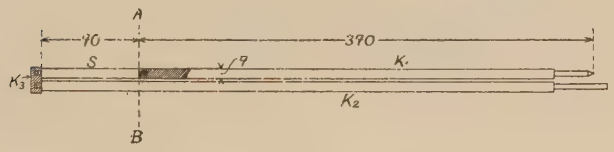
¶ K. Honda, Sci. Rep. vi. p. 204 (1917).

** S. Kaya, Sci. Rep. (1925-1926).

The furnace worked in a vacuum and gave a sufficient length of uniform heating at very high temperatures, say a maximum variation of only 2° along the length of 70 mm. at 1300° C. The specimens were cylindrical rods, 6 mm. in diameter and 70 mm. in length, made of armco iron. The linear magnification of the apparatus was 1200, so that at the A_3 point a sharp discontinuous deflexion of scale by about 24 centimetres was observed. But, owing to the yielding of the silica tubes used in the apparatus at very high temperatures, this apparatus could not be used beyond 1200° C.

After several fruitless trials, a differential method was adopted, a short description of which will be necessary. The specimen and the neutral were connected to form a differential dilatometric couple, as shown in fig. 1. For the neutral metallic cobalt was chosen, because it has no transformation in the vicinity of 900° and 1400°, and its coefficient of expansion, specific heat, and melting-point are of nearly the same values as those of pure iron. In the figure, two rods K_1 and K_2 are cobalt neutrals, having the same diameter as that of specimen S. S, K_1 and K_2, and a piece of cobalt K_3 are tightly screwed together in the form of a hair-pin,

Fig. 1.



leaving a clearance of about 1 mm. between the two parallel rods. If this pair of connected rods be introduced into the heating furnace so as to heat the left portion of AB sufficiently uniformly and its left end K_3 be lightly supported, the differential elongation between the iron and cobalt rods will cause a relative displacement between the ends of K_1 and K_2 rods. This displacement can be measured if the right end of K_2 rod be clamped and the same end of K_1 rod be lightly supported and its motion transmitted to a mirror system.

Fig. 2 shows the mirror system. The right end of K_2 rod is clamped to the base B by a screw C, and the coned end of K_1 rod touches the end of a quartz tube Q, which is co-axially fixed to a cylindrical rod W. W rests on a horizontal roller R_1 and is guided by two vertical rollers R_2 and R_3. Hence a displacement of the coned end can be observed as the

deflexion of a small mirror M attached to R_1. J is a screw for adjusting the mirror to the zero position.

Fig. 2.

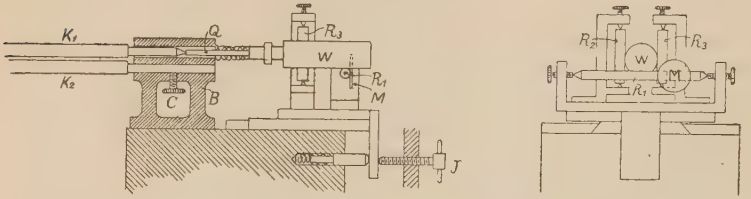
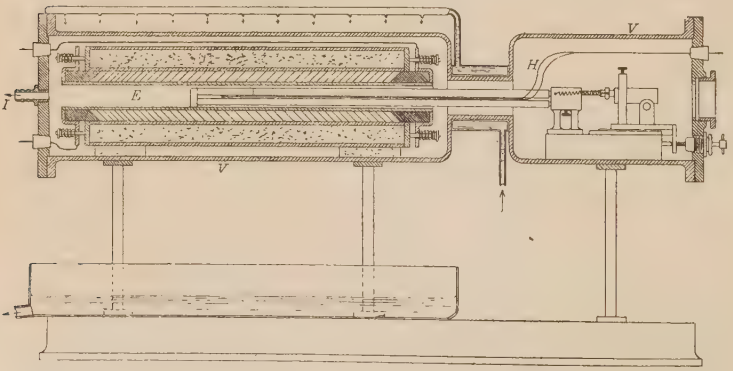


Fig. 3 shows the general arrangement of the apparatus ; here the electric furnace, the connected rods, and the mirror system, etc., are put into a closed vessel V, equipped with a water-cooling device. This vessel is connected with a pump through outlet I, and the heating and cooling of the specimen can be done in a vacuum. The temperature of the specimen is measured by a Le Chatelier thermocouple H. E is the carbon ring electric furnace as stated above.

Fig. 3.



If r be the radius of the horizontal roller and D be the scale distance, the relative change of length between the specimen and the neutral, that is, $\delta l - \delta l_0$, is given by

$$\delta l - \delta l_0 = r\theta,$$

where θ is the deflexion angle of the mirror. Further, if n be the scale deflexion, we have

$$\tan 2\theta = \frac{n}{\mathrm{D}} \doteqdot 2\theta,$$

$$\therefore \quad \delta l - \delta l_0 \doteqdot \frac{rn}{2\mathrm{D}}.$$

In the present case,

$$r = 2{\cdot}50 \text{ mm.}; \quad D = 1500 \text{ mm.}$$

$$\delta l - \delta l_0 = \frac{n}{1200} \text{ mm.}$$

The test specimens were cylindrical rods, 7 mm. in diameter and 70 mm. in length. They were made from electrolytic iron melted in a vacuum furnace. The result of the chemical analysis is given below :—

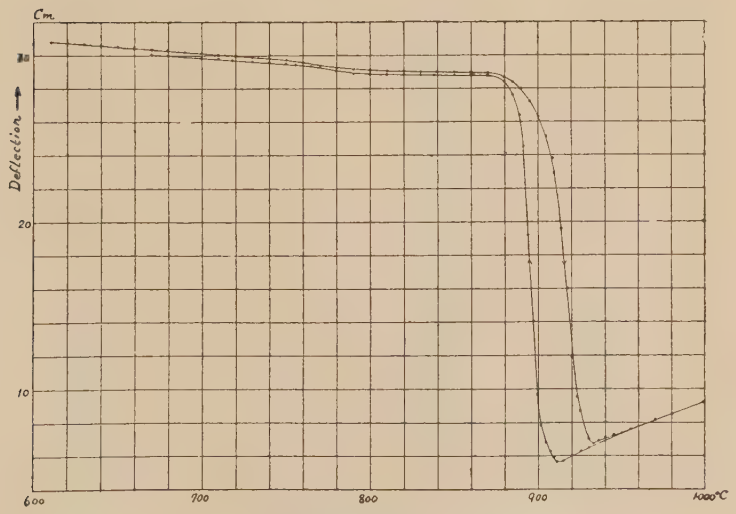
TABLE I.

C (%).	Si (%).	Mn (%).	S (%).	P (%).	Cu (%).
0·006	nil	trace	0·006	nil	nil

§ 3. *Results of Experiment.*

The change of length during the A_3 transformation was first

Fig. 4.



A_3 transformation.

observed, a typical result of which is given in fig. 4, and in Table II. In the figure, the ordinate represents the scale deflexion and the abscissa the temperature.

TABLE II.

Temperature in deg. C.	Scale Deflexion in cm.	Temperature in deg. C.	Scale Deflexion in cm.
(Heating)		950	7·36
610	30·80	955	7·60
620	30·75	959	7·80
630	30·70	970	8·20
640	30·60	980	8·50
650	30·50	1000	9·20
660	30·45		
670	30·35	(Cooling)	
680	30·30	960	7·75
690	30·20	940	6·90
700	30·15	930	6·50
710	30·05	925	6·30
720	30·00	920	6·00
730	29·87	915	5·70
740	29·81	911	5·62
750	29·76	909	5·90
760	29·59	907	6·30
770	29·40	904	6·80
780	29·24	901	7·80
790	29·15	899	9·70
800	29·10	897	14·00
810	29·04	894	19·20
820	29·01	891	24·50
830	29·00	889	26·40
840	29·00	885	27·60
850	29·00	880	28·40
860	29·00	870	28·80
870	28·94	860	28·80
880	28·69	850	28·80
885	28·40	838	28·80
890	28·00	830	28·80
895	27·20	820	28·80
900	26·30	810	28·80
905	25·10	800	28·80
909	23·80	790	28·85
910	22·90	780	29·06
914	19·60	765	29·36
918	16·00	756	29·40
920	11·90	750	29·41
923	9·50	730	29·60
925	8·70	718	29·70
930	7·00	710	29·80
933	6·70	700	29·83
936	6·95	690	29·90
940	7·10	680	30·00
945	7·23	670	30·05

From fig. 4 we take the scale deflexion due to the A_3 transformation to be

$$n = 240 \text{ mm.}$$

$$\therefore \quad \delta l - \delta l_0 = \frac{240}{1200} = 0{\cdot}200 \text{ mm.}$$

As the transformation proceeds at a constant temperature, so that

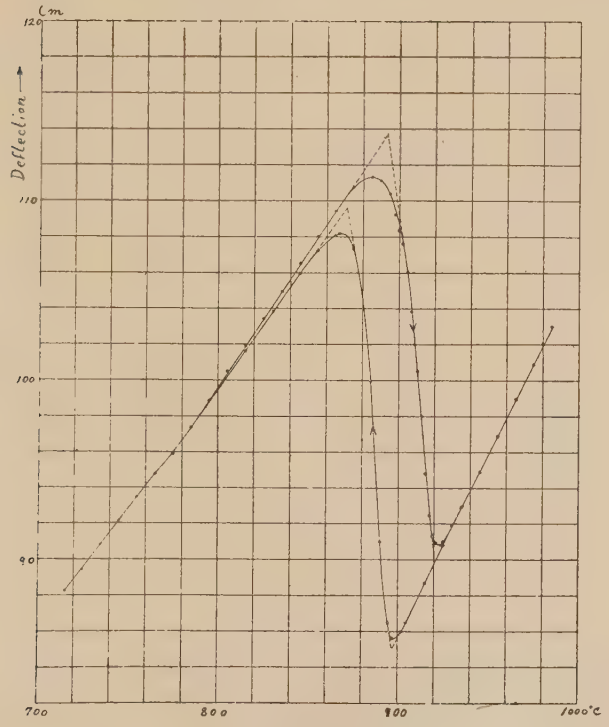
$$\delta l_0 = 0,$$

$$\therefore \quad \delta l = 0{\cdot}200 \text{ mm.}$$

Next, in order to see the effect of the screwed parts (3·5 mm. thick, 4 mm. long, and $\frac{1}{3}\frac{1}{2}$ inch pitch) on the value of δl, the following experiment was made :—

Cylindrical specimens of the same length and diameter, *i. e.*, 70×7 mm., and of the same material but without the screw ends were prepared, and the change of length due to the A_3 transformation was measured by using the total dilatometer already mentioned. Fig. 5 shows an example of

Fig. 5.



A_3 transformation.

such measurement. Hence we take

$$n \doteqdot 240 \text{ mm.}$$

$$\therefore \quad \delta l \doteqdot 0{\cdot}200 \text{ mm.}$$

i. e., exactly the same result as before. Hence it is to be concluded that the effect of the screwed parts on the change of length is not appreciable.

Let l_α be the length of the specimen just below the A_3 point and let l_γ be the length of the specimen just above the A_3 point, then we have :—

$$l_\alpha = l_\gamma + \delta l,$$

$$\therefore \quad \frac{l_\alpha}{l_\gamma} = 1 + \frac{\delta l}{l_\gamma},$$

and l_γ can be deduced from the initial length and the scale deflexion at 920° in fig. 5, thus :—

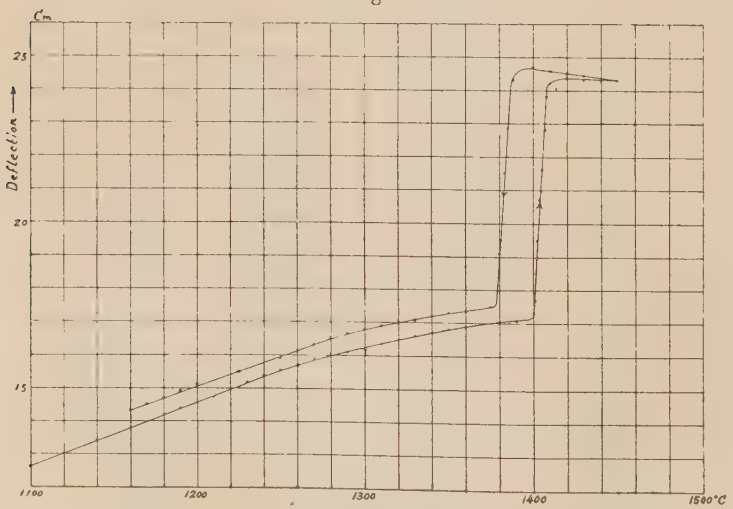
$$n = 900 \text{ mm.}$$

$$\therefore \quad l_\gamma = 70{\cdot}0 + \frac{900}{1200} = 70{\cdot}75 \text{ mm.}$$

$$\frac{\delta l}{l_\gamma} = \frac{0{\cdot}200}{70{\cdot}75} = 0{\cdot}00282.$$

Next the heating was further continued to as high as 1390° C. ; but in this range no abnormal change of length was observed, γ-iron continuously expanding with the rise of temperature, at a rate greater than that of α-iron. As the temperature reaches 1400° an abrupt increase of length is observed, as shown in fig. 6 and Table III.

Fig. 6.



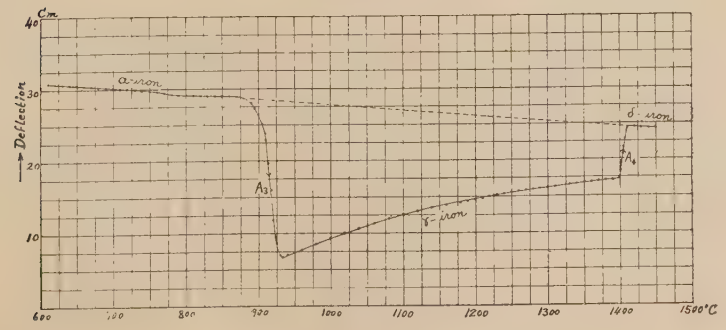
A_4 transformation.

This increase is due to the A_4 transformation. When this discontinuous change has been completed the rate of expansion becomes less than that in the γ-region, and the deflexion-temperature curve lies in the prolongation of that in α-iron, as shown in fig. 7.

TABLE III.

Temperature in deg. C.	Scale Deflexion in cm.	Temperature in deg. C.	Scale Deflexion in cm.
(Heating)		1408	23·80
1000	9·25	1410	24·20
1020	10·00	1420	24·35
1040	10·70	1430	24·30
1060	11·40	1440	24·30
1080	12·10	1450	24·30
1100	12·60		
1120	13·00	(Cooling)	
1140	13·40	1450	24·30
1160	13·80	1440	24·30
1180	14·20	1430	24·45
1190	14·40	1420	24·50
1200	14·60	1410	24·60
1210	14·71	1400	24·70
1220	15·00	1388	24·30
1230	15·20	1385	22·85
1240	15·40	1383	21·50
1250	15·54	1380	19·10
1260	15·70	1375	17·50
1270	15·90	1360	17·35
1280	16·09	1350	17·30
1290	16·10	1340	17·20
1300	16·20	1330	17·10
1310	16·35	1320	17·00
1320	——	1310	16·90
1330	16·60	1300	16·80
1340	16·70	1290	16·65
1350	16·80	1280	16·50
1360	16·90	1270	16·30
1370	17·00	1260	16·10
1380	17·05	1250	15·90
1390	17·10	1225	15·50
1400	17·30	1200	15·10
1401	17·90	1190	14·90
1402	19·50	1180	14·70
1403	20·70	1170	14·50
1405	21·60	1160	14·30
1407	22·80		

Fig. 7.



This fact confirms the conclusion that δ-iron is the same as α-iron. During cooling, the reversed change takes place at the Ar_4 point, which lies a little below the Ac_4 point, *i. e.*, about 20 degrees.

From fig. 6 the scale deflexion during the A_4 transformation is taken to be

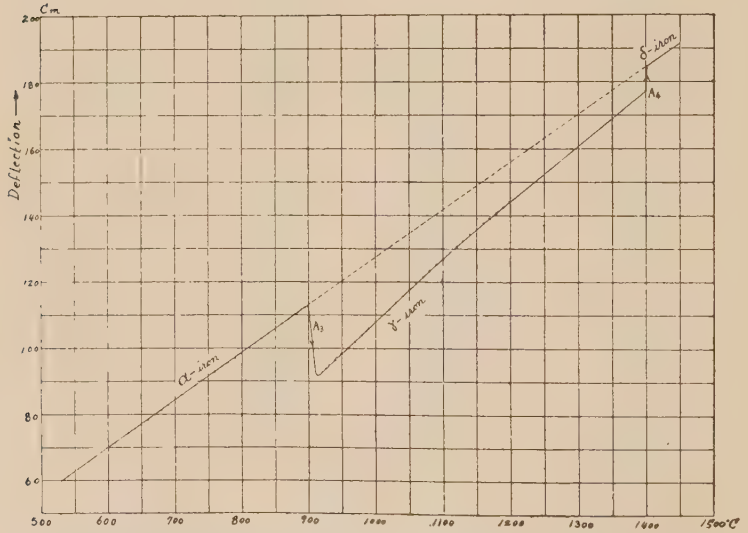
$$n = 73{\cdot}0 \text{ mm.},$$

and therefore

$$\delta l = \frac{73{\cdot}0}{1200} = 0{\cdot}0608 \text{ mm.}$$

Fig. 8 shows an example of the expansion-temperature curve obtained by the total dilatometer. In this case, however, observation beyond 1200° was not possible as stated above; but if the heating curves of both α- and γ-irons

F



be produced to 1400° C., the difference between the ordinates of these curves at this temperature gives an expansion of 73 mm. corresponding to the A_4 transformation which is in satisfactory agreement with the observed value.

If l_γ be the length of specimen just below the Ac_4 point, and l_δ be the length of specimen just above the Ac_4 point, we have

$$l_\delta = l_\gamma + \delta l,$$

$$\therefore \quad \frac{l_\delta}{l_\gamma} = 1 + \frac{\delta l}{l_\gamma}.$$

From the initial length and the scale deflexion given in fig. 8, we obtain

$$l_\gamma = 70{\cdot}0 + \frac{1770}{1200} = 71{\cdot}47 \text{ mm.}$$

$$\therefore \quad \frac{\delta l}{l_\gamma} = \frac{0{\cdot}0608}{71{\cdot}47} = 0{\cdot}000851.$$

§ 4. *Comparison of the Results of Experiment with that of X-Ray Analysis.*

Let a_α be the lattice parameter of α-iron just below the A_3 point, and a_γ be the lattice parameter of γ-iron just above the A_3 point; then one side of an elementary cube occupied by one atom of either α- or of γ-iron is respectively given by

$$\frac{a_\alpha}{\sqrt[3]{2}} \quad \text{and} \quad \frac{a_\gamma}{\sqrt[3]{4}},$$

and the difference between these two is evidently the contraction or expansion due to the A_3 transformation.

Similarly, if a_δ be the lattice parameter of δ-iron just above the A_4 point, and a_γ be the lattice parameter of γ-iron just below the A_4 point, then the difference between $\frac{a_\delta}{\sqrt[3]{2}}$ and $\frac{a_\gamma}{\sqrt[3]{4}}$ shows the expansion or contraction due to the A_4 transformation.

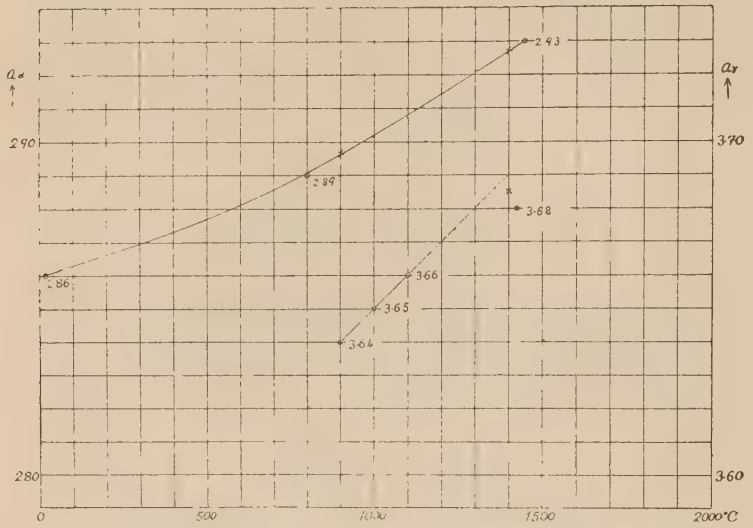
According to Westgren, the values of a_α and a_γ are as follows:—

Table IV.

Temperature.	a_α(Å).	Temperature.	a_γ(Å).
20° C.	2·86	1000° C.	3·65
800° C.	2·89	1100° C.	3·66
1450° C.	2·93	1425° C.	3·68

The lattice parameters just below and above the A_3 and A_4 points are not given in the table, but they can be found from fig. 9.

Fig. 9.



Thus, at the A_3 point we have

$$a_\alpha = 2{\cdot}897 \text{ Å} ; \quad a_\gamma = 3{\cdot}640 \text{ A},$$

$$1 + \frac{\delta l}{l_\gamma} = \frac{2{\cdot}897}{3{\cdot}640} \times 1{\cdot}2599 = 1{\cdot}00273,$$

or

$$\frac{\delta l}{l_\gamma} = 0{\cdot}00273,$$

which is in close agreement with the observed value

$$\frac{\delta l}{l_\gamma} = 0{\cdot}00282.$$

Again, at the A_4 point we have

$$a_\alpha = 2{\cdot}927\text{Å}, \quad a_\gamma = 3{\cdot}685 \text{ Å} ;$$

and hence

$$\frac{\delta l}{l_\gamma} = 0{\cdot}000767,$$

which is also in close agreement with the observed value

$$\frac{\delta l}{l_\gamma} = 0{\cdot}000851.$$

§ 5. *Summary.*

The present investigation may be summarized as follows:—

(1) In the case of pure iron, during heating, the A_4 transformation is accompanied by an expansion and the A_3 transformation by a contraction, and during cooling these changes are reversed.

(2) The ratio of the magnitudes of the change of length due to the A_3 and A_4 transformations is about 10 : 3.

(3) The thermal dilatation curve of δ-iron forms the continuation of that of α-iron, showing that δ-iron is the same as α-iron.

The writer wishes to express his cordial thanks to Professor K. Honda, under whose kind guidance the present investigation was carried out, and also to Professors T. Ishiwara and M. Yamada for their valuable advice during the course of the present investigation. He is also much indebted to Lecturer S. Kaya for the construction of the electric furnace.

XC. *Germanium in a British Mineral.* *By* Walter Scutt, *H.M. Inspector, Board of Education* *.

THE occurrence of a noticeable percentage of the very rare element germanium in a British mineral has apparently not been recorded previously. Prof. Hartley, of Dublin, in 1897, writing on "The Wide Dissemination of some of the Rarer Elements" (Journ. Chem. Soc. vol. lxxi. pt. i. p. 533), notes the presence of gallium, indium, and thallium in a variety of British minerals ; but he makes no reference to germanium (which had been discovered in 1886 by Winkler in a new silver mineral, Argyrodite, from the Himmelfürst mine near Freiburg, Saxony).

The standard text-books on mineralogy state that germanium is found in appreciable quantities only in the scarce Bolivian minerals Argyrodite ($4Ag_2S$, GeS_2), containing 6–7 per cent. Ge, and Canfieldite ($4Ag_2S$, $(SnGe)S_2$), containing 1·8 per cent. Ge. To these must now be added Germanite, a sulphide of copper, iron, and germanium, found at Tsumeb in South-West Africa (O. Pufahl, 1922, *Metall und Erz*, Halle, vol. xix. p. 324). This contains about 5–8 per cent. of germanium.

* Communicated by the Author.

In these three minerals germanium is associated with a large percentage of either silver or copper ; but the position of germanium (atomic number 32) in the Periodic Table would suggest the greater probability of its occurrence in association with zinc (atomic number 30). It therefore seemed to me worth while to make a spectroscopic search for germanium in a number of specimens of zinc blende. The spectrograph used for the purpose is one of my own construction, with a good concave grating of 2 metres radius of curvature, ruled on the Blythswood engine at the National Physical Laboratory, and giving a first-order spectrum which can be photographed on two 12-inch films covering the range from λ 7699·3 K to λ 2293·9 Cu. This instrument is much simpler in construction than either Rowland's or Eagle's mounting, embodying a plan similar to one of those described by Wadsworth (Astrophys. Journ. vol. ii. (1895), p. 370 ; and vol. iii. (1896), p. 46), first suggested to me by Prof. A. Fowler. Both the grating and the photographic film are fixed, and the slit is mounted on a movable radius-arm one metre in length, with a simple automatic arrangement for keeping the plane of the slit at right angles to the line joining the light-source and the centre of the grating.

For producing the spectra, specially pure carbons were cored in the usual way with the powdered minerals, the cored carbon being used as the positive pole of an arc run from the 220-volts D.C. mains through a resistance reducing the current to 2 or 3 amperes.

The spectra of various specimens of blende from Cornwall, Cumberland, and Derbyshire were photographed, and it was found, as one would expect, that the finer, better crystallized, and more attractive the specimen, the less likely was it to contain any of the rarer elements, though cadmium was usually present. On the other hand, some specimens of uninteresting appearance showed traces of one or more of the elements gallium, indium, and thallium (as recorded by Hartley) ; but no trace of germanium was found until a specimen of blende from Wales was examined. This was a dark grey, uncrystallized lump possessing very little lustre, obtained by the writer from an old lead mine in the neighbourhood of Devil's Bridge, Aberystwyth.

Referring to the photograph reproduced, it will be seen that the spectrum of this blende clearly reveals the presence of more than a trace of germanium. The photograph gives the portion of the ultra-violet in which most of the lines of Ge occur, the spectrum of the blende (2) being placed between comparison spectra of zinc (1) and Germanite (3).

Both Germanite and Blende distinctly show the following Ge lines:—3269·5 (between Cd 3261 and Cu 3274); 3039·1 (the least refrangible of a trio, the other two lines being Zn 3036 and Fe 3037·4); 2754·7 (near Zn 2756·5); 2709·7 (near Zn 2712·6); 2691·4; 2651·7/1·3 (seen separate on film with magnifier); and 2592·6.

On comparing the spectrum of Germanite with that of the Blende it will be noted that the relative intensity of the Ge lines in the two spectra is about 2 to 1. Consequently, the exposures having been equal, it is probable that this particular specimen of zinc blende contains from 2 to 4 per cent. of germanium, which is greater than the percentage in Canfieldite. Unfortunately, a direct comparison spectrum of the latter is not given in the photograph, for all my efforts to obtain specimens of Argyrodite and Canfieldite have been fruitless, while the cost of pure germanium metal (£8 5*s.* a gramme) is prohibitive); but, through the kindness of Dr. Prior, of the Natural History Museum, who informed me of the discovery of Germanite, I was able to get a specimen of this mineral from a London dealer, and this has furnished the interesting comparison seen in the photograph.

London, W. 3.
February, 1926.

XCI. *The Reflexion of X-Rays from Crystals.*

By R. Schlapp, *Ph.D.* (*Camb.*), *University of Edinburgh* *.

1. *Introduction.*

THE purpose of the following paper is to give an account of the principal phenomena of the X-ray optics of perfect crystals on the basis of the electromagnetic theory of light in continuous media. The method depends on the solution of the equations of propagation of electromagnetic disturbance in a medium whose specific inductive capacity is a periodic function of position. The simplest medium of this type, and the one most amenable to mathematical treatment, is the periodically stratified medium, in which the specific inductive capacity is a periodic function of distance from a given plane. Such a medium appears to suffice for the description of the phenomena under consideration, for the present analysis will be found to reproduce most of the features of propagation and reflexion of X-rays in

* Communicated by Professor C. G. Darwin, F.R.S.

crystals which have emerged in discussions of the problem by other methods.

The analysis is, of course, applicable without much modification to other instances of selective reflexion due to stratified structure, as, for example, the crystals of chlorate of potash studied by Stokes * and by Rayleigh †, or the films prepared by Lippmann's process of colour photography ‡. As a typical problem of this class, Rayleigh § investigated the transverse vibrations of a string of periodically distributed density; he was led in this connexion to the differential equation of G. W. Hill, an equation with periodic coefficients, but the solutions which had previously been developed in view of astronomical applications were not well adapted to the physical problem. More recently Hill's equation has been dealt with by methods initiated by E. T. Whittaker, which are peculiarly suited to the present problem, and allow a complete solution to be worked out.

2. *The Equations of Propagation.*

The circuital relations of the field may be written

$$-(\dot{\alpha}\dot{\beta}\dot{\gamma}) = \text{curl}\,(\text{PQR}),$$

$$\frac{\text{K}}{c^2}(\dot{\text{P}}\dot{\text{Q}}\dot{\text{R}}) = \text{curl}\,(\alpha\beta\gamma),$$

where (PQR), $(\alpha\beta\gamma)$ denote the electric and magnetic intensities at a point of the medium at which the specific inductive capacity is K, c the ratio of the electromagnetic to the electrostatic unit of charge, and a dot differentiation with respect to time. The magnetic permeability of the medium is taken as unity. These relations lead to the following equations of propagation of the electric and magnetic intensities :

$$\frac{\text{K}}{c^2}(\ddot{\text{P}}\ddot{\text{Q}}\ddot{\text{R}}) = -\text{curl curl}\,(\text{PQR}),$$

$$\frac{1}{c^2}(\ddot{\alpha}\ddot{\beta}\ddot{\gamma}) = -\text{curl}\,\frac{1}{\text{K}}\,\text{curl}\,(\alpha\beta\gamma),$$

together with

$$\text{div}(\text{KP}\,\text{KQ}\,\text{KR}) = 0,$$

$$\text{div}(\alpha\beta\gamma) = 0.$$

* G. G. Stokes, Proc. Roy. Soc. xxxviii. p. 174 (1885).
† Rayleigh, Phil. Mag. xxvi. p. 256 (1888).
‡ H. E. Ives, Astrophys. J. xxvii. p. 325 (1908).
§ Rayleigh, Papers, vol. iii. p. 1.

Now suppose that the plane $y=0$ is taken parallel to the stratifications of the medium, so that K is a function of y alone. Then one solution of the propagation equations is given by an electric vector (00R), provided R satisfies

$$\frac{\partial^2 \mathrm{R}}{\partial x^2}+\frac{\partial^2 \mathrm{R}}{\partial y^2}=\frac{\mathrm{K}}{c^2}\frac{\partial^2 \mathrm{R}}{\partial t^2},$$

and a second is given by (00γ), provided γ satisfies

$$\frac{\partial}{\partial x}\frac{1}{\mathrm{K}}\frac{\partial \gamma}{\partial x}+\frac{\partial}{\partial y}\frac{1}{\mathrm{K}}\frac{\partial \gamma}{\partial y}=\frac{1}{c^2}\frac{\partial^2 \gamma}{\partial t^2}.$$

These two solutions represent fields polarized respectively in and perpendicular to the xy-plane, which may be taken as the plane of propagation, and accordingly furnish a basis for discussing the propagation of radiation of any state of polarization in the stratified medium.

Assuming R and γ to be of the form $\mathrm{R}'e^{i(pt-\alpha x)}$ and $\gamma' e^{i(pt-\alpha x)}$ respectively, we obtain the following equations for R′ and γ':

$$\frac{d^2\mathrm{R}'}{dy^2}+\left(\frac{p^2}{c^2}\mathrm{K}-\alpha^2\right)\mathrm{R}'=0, \quad . \quad . \quad (2{\cdot}1)$$

$$\mathrm{K}\frac{d}{dy}\frac{1}{\mathrm{K}}\frac{d\gamma'}{dy}+\left(\frac{p^2}{c^2}\mathrm{K}-\alpha^2\right)\gamma'=0.$$

The second of these may be transformed by the substitution of a new dependent variable v, given by $\gamma'=v\sqrt{\mathrm{K}}$. If we suppose the fluctuations of the specific inductive capacity to be small in comparison with its mean value, so that

$$\mathrm{K}=\mathrm{K}_0(1+h),$$

where h is so small that its squares and higher powers may be neglected, we find that the equation to be satisfied by v is

$$\frac{d^2v}{dy^2}+\left(\frac{p^2}{c^2}\mathrm{K}-\alpha^2+\frac{1}{2}\frac{d^2h}{dy^2}\right)v. \quad . \quad . \quad . \quad (2{\cdot}2)$$

In the equations (2·1) and (2·2), K may be supposed to be expanded in a Fourier's series whose period is d, the distance between the stratifications

$$\mathrm{K}=\mathrm{K}_0+\mathrm{K}_1\cos\frac{2\pi y}{d}+\mathrm{K}_2\cos\frac{4\pi y}{d}\ldots$$

$$+\mathrm{K}_1'\sin\frac{2\pi y}{d}+\mathrm{K}_2'\sin\frac{4\pi y}{d}\ldots, \quad . \quad (2{\cdot}3)$$

where the constants $\mathrm{K}_1\,\mathrm{K}_2\ldots\mathrm{K}_1'\,\mathrm{K}_2'\ldots$, which determine

the amplitude of the fluctuation of K, are small in comparison with the mean value K_0 of the specific inductive capacity. All the coefficients of K will be supposed real; that is, the crystal will be regarded as perfectly transparent. For ordinary crystals and X-ray frequencies K_0 will be very slightly less than unity.

If a new independent variable η be introduced in place of $\frac{\pi y}{d}$, R′ and v are seen to satisfy an equation which is of the same form in both cases, viz.

$$\frac{d^2u}{d\eta^2} + [\Psi_0 + 2\Psi_1 \cos(2\eta + \delta_1) + 2\Psi_2 \cos(4\eta + \delta_2) + \ldots]\, u = 0, \quad \ldots \quad (2{\cdot}4)$$

where

$$\Psi_0 = \left(\frac{pd}{\pi c}\right)^2 K_0 - \left(\alpha \frac{d}{\pi}\right)^2,$$

$$\delta_r = -\arctan \frac{K_r'}{K_r},$$

when $u = R'$ or $u = v$, while the coefficients Ψ_r $(r \neq 0)$ are given by

$$\Psi_r = \frac{1}{2}\left(\frac{pd}{\pi c}\right)^2 \sqrt{K_r^2 + K_r'^2}, \qquad \text{when } u = R', \quad (2{\cdot}5)$$

and

$$\Psi_r = \frac{1}{2}\left\{\left(\frac{pd}{\pi c}\right)^2 - \frac{2r^2}{K_0}\right\} \sqrt{K_r^2 + K_r'^2}, \quad \text{when } u = v. \quad (2{\cdot}6)$$

Thus in the present problem $\Psi_1, \Psi_2 \ldots$ are constants, while Ψ_0 is a variable parameter depending on α. It will be seen below how the character of the solution depends on the value of Ψ_0.

The equation (2·4) resembles the equation introduced in connexion with Lunar Theory by G. W. Hill *, and commonly known by his name, but it is more general in that all the periodic terms may be affected with phase constants.

3. *Solution of the Equations of Propagation.*

The general theory of differential equations with periodic coefficients shows that a particular solution of the present equation is of the form $e^{\mu\eta}\phi(\eta)$, where $\phi(\eta)$ is a periodic function of period 2π, and μ and the coefficients of ϕ depend on the constants of the equation. Since the equation is

* See Whittaker & Watson, 'Modern Analysis,' § 19.12.

unaltered by writing $-\eta$ for η, and $-\delta_r$ for δ_r, another particular solution is $e^{-\mu'\eta}\phi'(-\eta)$, where μ' is derived from μ and the coefficients of ϕ' from those of ϕ by writing $-\delta_r$ for δ_r. These two solutions may be taken as fundamental solutions, so that the general solution is of the form

$$u = Ae^{\mu\eta}\phi(\eta) + Be^{-\mu'\eta}\phi'(-\eta),$$

where A and B are constants.

We shall try to satisfy the equation (2·4), when

$$\Psi_0 = a_0 + a_1\Psi_1 + a_2\Psi_2 \ldots,$$

by an expression of the form

$$u = e^{\mu\eta}(1 + b_1\Psi_1 + b_2\Psi_2 + \ldots),$$

where $a_1\, a_2 \ldots$ are constants, and $b_1\, b_2 \ldots$ are periodic functions of η. Terms involving powers of the small quantities $\Psi_1\, \Psi_2 \ldots$ higher than the first have not been written down. If we substitute these values of u and Ψ_0 in the left-hand member of the equation, the coefficients of all powers of $\Psi_1\, \Psi_2 \ldots$ must vanish separately. The constant term gives $a_0 = -\mu^2$, while that in Ψ_r gives

$$b_r'' + 2\mu b_r' + a_r + 2\cos(2r\eta + \delta_r) = 0.$$

Since b_r is to be a periodic function of η, a_r must vanish, so that to the present degree of approximation $\Psi_0 = -\mu^2$ and

$$b_r = \frac{1}{2}\left[\frac{\cos(2r\eta + \delta_r)}{r^2 + \mu^2} - \frac{\mu \sin(2r\eta + \delta_r)}{r(r^2 + \mu^2)}\right].$$

Hence a particular solution of the equation (2·4) is

$$u = e^{\sqrt{-\Psi_0}\,\eta}\left[1 + \tfrac{1}{2}\Sigma\left\{\frac{\cos(2r\eta + \delta_r)}{r^2 + \mu^2} - \frac{\mu \sin(2r\eta + \delta_r)}{r(r^2 + \mu^2)}\right\}\Psi_r\right].$$

The convergence of this solution breaks down when $-\mu^2 = r^2$, that is, when Ψ_0 is near a squared integer ; it is, however, valid when Ψ_0 is numerically small. Under these circumstances what may be called the zero-order solution can be written

$$u = e^{\sqrt{-\Psi_0}\cdot\eta}\left[1 + \tfrac{1}{2}\Sigma\frac{\Psi_r \cos(2r\eta + \delta_r)}{r^2 - \Psi_0}\right]. \quad . \quad (4·1)$$

Thus for values of $\Psi_0 \geq 0$ the solution is periodic, while for $\Psi_0 < 0$ it is affected with a real exponential factor.

The convergence difficulty when Ψ_0 is near a squared integer may be overcome by using the method of solution devised by Whittaker * in connexion with the equation of

* E. T. Whittaker, Proc. Edin. Math. Soc. xxxii. p. 75 (1914).

Mathieu, to which the present equation reduces if all the constants vanish except Ψ_0 and Ψ_1. Whittaker's solution is again of the form $e^{\mu\eta}\phi(\eta)$, but, unlike the previous solution, is applicable in the vicinity of $\Psi_0=r^2$; but the way in which μ and the coefficients of ϕ depend on the constants $\Psi_0\,\Psi_1\,\Psi_2\ldots$ of the equation is so complicated that it is not practicable to express them directly in terms of these constants. The solution depends on the introduction of an intermediate parameter σ; the quantities Ψ_0, μ, and the coefficients of ϕ are then expressible in a conveniently simple form in terms of σ and $\Psi_1\,\Psi_2\ldots$.

Following Whittaker, we try to determine a solution of the equation (2·4) when Ψ_0 is near a squared integer n^2, of the form $e^{\mu\eta}\phi(\eta)$, where

$$\begin{aligned}\mu &= \kappa_1\Psi_1+\kappa_2\Psi_2+\ldots,\\ \phi &= \sin(n\eta-\sigma)+\mathrm{A}_1\Psi_1+\mathrm{A}_2\Psi_2+\ldots,\\ \Psi_0 &= n^2+\alpha_1\Psi_1+\alpha_2\Psi_2+\ldots.\end{aligned}$$

As before, terms of the second or higher order in the small quantities $\Psi_1\,\Psi_2\ldots$ are omitted. The κ's and α's are functions of the parameter σ, and the A's are functions of η and σ, which are now to be determined. The parameter σ is not restricted to be real. It will be observed that this solution reduces to the solution

$$u=\sin(n\eta-\sigma)$$

of the corresponding equation

$$\frac{d^2u}{d\eta^2}+n^2u=0$$

when $\Psi_1\,\Psi_2\ldots=0$.

If these expressions be substituted in the differential equation, and successive powers of each of the coefficients $\Psi_1\,\Psi_2\ldots$ equated to zero, certain relations are found, which are sufficient to determine the κ's, A's, and α's, if the assumption is made that the functions $\mathrm{A}_1\,\mathrm{A}_2\ldots$ do not contain terms in $\cos(n\eta-\sigma)$ or $\sin(n\eta-\sigma)$. In this way the terms linear in Ψ_r give

$$\left.\begin{aligned}\alpha_r=\kappa_r&=0,\\ \mathrm{A}_r&=\frac{\sin\{(n+2r)\eta-\sigma+\delta_r\}}{4r(r+n)}+\frac{\sin\{(n-2r)\eta-\sigma-\delta_r\}}{4r(r-n)}\end{aligned}\right\}(r\neq n),$$

$$\alpha_n=\cos(2\sigma+\delta_n),\qquad \kappa_n=\frac{1}{2n}\sin(2\sigma+\delta_n),$$

$$\mathrm{A}_n=\frac{\sin(3n\eta-\sigma+\delta_n)}{8n^2}.$$

The solution of the equation (2·4) when

$$\Psi_0 = n^2 + \Psi_n \cos(2\sigma + \delta_n)$$

is accordingly, to the first power of Ψ_r,

$$u = e^{\frac{1}{2n}\Psi_n \sin(2\sigma+\delta_n)\,.\,\eta}\left[\sin(n\eta-\sigma) + \Sigma\frac{\sin\{(n+2r)\eta-\sigma+\delta_r\}}{4r(r+n)}\Psi_r + \Sigma'\frac{\sin\{(n-2r)\eta-\sigma-\delta_r\}}{4r(r-n)}\Psi_r\right], \quad (4\cdot2)$$

where the summations are from $r=1$ to $r=\infty$, and Σ' omits $r=n$. This will be referred to as the nth order solution. We may observe in passing that for a given n, Ψ_0 and the exponential factor in u are determined, within the limits of the present approximation, solely by Ψ_n.

The form of the solution shows that u is periodic when $\sin(2\sigma+\delta_n)$ vanishes; the corresponding critical values of Ψ_0 are $n^2 \pm \Psi_n$, which lie in the neighbourhood of the squared integers. We have already seen that $\Psi_0 = 0$ is another critical value for which the solution becomes periodic; and examination shows that for values of Ψ_0 between $-\infty$ and 0, or between the two critical values associated with a squared integer, the index of the exponential factor in the solution is real, while for all other values of Ψ_0, the index is imaginary.

The two cases correspond respectively to a disturbance decaying or increasing exponentially, and to a periodic disturbance of constant amplitude.

It is, of course, possible to pursue the solution to any desired degree of approximation; but for the physical problem, the present approximation in which squares of Ψ_r are rejected is sufficiently close.

4. *Propagation in the Interior of the Crystal.*

The disturbance in the stratified medium is given by a solution of the equation (2·4) multiplied by an exponential factor $e^{i(pt-ax)}$, subject to Ψ_0 having the appropriate value. The simplest form of propagation in an unlimited stratified medium accordingly consists of a sheaf of plane waves travelling forwards as well as backwards along a discrete series of directions. One of these waves, corresponding to the predominant term in the solution of the generalized Hill's equation, travels with approximately the velocity of light, and is of predominant amplitude; the amplitudes of the waves corresponding to the subsidiary terms of the solution fall off as their direction deviates more from that of

the predominant wave, and their velocities likewise diverge from the normal value, those on one side travelling faster and those on the other side slower. Thus the phase velocity of part of the disturbance is greater than the velocity of light *in vacuo*; such a velocity is admissible, as it applies to the phase of a permanent state of propagation, and not to a disturbance seeking fresh ground.

For certain directions of propagation the interior disturbance is affected with an exponential damping factor causing decay to $1/e$ after penetrating a distance

$$\frac{2nd}{\pi\Psi_n \sin(2\sigma + \delta_n)};$$

this distance attains its minimum value $\frac{2nd}{\pi\Psi_n}$ when

$$2\sigma + \delta_n = \frac{\pi}{2},$$

that is, when $\Psi_0 = n^2$. The damping factor clearly represents the effect of partial reflexions from the successive strata in robbing the primary beam, incident at the proper angle, of its energy, while the reflected beam is correspondingly enhanced. The transfer of energy between the two beams is effected, as Darwin showed, by the multiple reflexions which take place between the strata, in the sense that portions of the primary beam which have suffered an even number of reflexions are travelling in the same direction as the primary beam, but have a retardation of an odd number of half wave-lengths on it, and interfere destructively with it; the energy so destroyed reappears, completely in the absence of ordinary absorption, in the reflected beam. Darwin's primary extinction is accordingly represented in the present analysis by the exponential factor affecting the solution of the generalized Hill's equation.

5. *Reflexion from the Face of a Stratified Medium of Infinite Depth.*

Suppose the medium to occupy all space on the negative side of the plane $y=0$, so that the face is parallel to the stratifications. Let plane waves, polarized in the plane of incidence, fall on the face in a given direction. The electric intensity R_1 outside the medium may then be written, apart from a factor $e^{i(pt-\alpha x)}$,

$$R_1 = Ae^{im\eta} + Be^{-im\eta}, \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

where A and B are constants, in general complex, giving

amplitude and phase of the incident and reflected waves, and m determines the glancing angle θ of incidence or reflexion in accordance with the equation

$$\sin\theta = m\frac{\pi c}{pd}.$$

Inside the medium the electric intensity is represented by one of the fundamental solutions of equation (2·4), that solution being chosen which gives a disturbance decaying as it penetrates the medium. This solution is determined by the value of Ψ_0, which in turn depends on m, and therefore on θ. Since the disturbance is propagated with velocity c outside the medium,

$$m^2 = \left(\frac{pd}{\pi c}\right)^2 - \left(\alpha\frac{d}{\pi}\right)^2$$

$$= \left(\frac{pd}{\pi c}\right)^2 (1-\mathrm{K}_0)+\Psi_0, \quad . \quad . \quad . \quad (5{\cdot}2)$$

so that

$$\sin^2\theta = 1-\mathrm{K}_0+\left(\frac{\pi c}{pd}\right)^2\Psi_0. \quad . \quad . \quad . \quad (5{\cdot}3)$$

Thus for real angles of incidence, Ψ_0 must be greater than $-\left(\frac{pd}{\pi c}\right)^2(1-\mathrm{K}_0)$, so that we may confine our attention to the zero-order solution (4·1) of equation (2·4), which is valid when Ψ_0 is numerically small, and to the solutions (4·2), valid when Ψ_0 has values near the squared integers.

For small values of the glancing angle θ, corresponding to small values of Ψ_0, we may write for the electric intensity inside the medium

$$\mathrm{R}_2 = \mathrm{D}e^{\sqrt{-\Psi_0}\,\eta}\left[1+\tfrac{1}{2}\Sigma\frac{\Psi_r}{r^2-\Psi_0}\cos(2r\eta+\delta_r)\right], \quad (5{\cdot}4)$$

where D is a complex constant, and a factor $e^{i(pt-\alpha x)}$ has been omitted as before. The solutions (5·1) and (5·4) are now to be fitted together in accordance with the usual boundary conditions of continuity of R and its gradient $\frac{\partial \mathrm{R}}{\partial\eta}$ across the interface $y=0$. These conditions give

$$\mathrm{A}+\mathrm{B} = \mathrm{D}u,$$

$$im(\mathrm{A}-\mathrm{B}) = \mathrm{D}[u\sqrt{-\Psi_0}-v],$$

where

$$u = 1+\tfrac{1}{2}\Sigma\frac{\Psi_r\cos\delta_r}{r^2-\Psi_0},$$

$$v = \Sigma\frac{r\Psi_r}{r^2-\Psi_0}\sin\delta_r.$$

On eliminating D, we obtain

$$\frac{B}{A} = \frac{i\beta - 1}{i\beta + 1}, \quad \ldots \ldots \quad (5{\cdot}5)$$

where

$$\beta = \frac{mu}{u\sqrt{-\Psi_0 - v}}.$$

For larger glancing angles, corresponding to

$$\Psi_0 = n^2 + \Psi_n \cos(2\sigma + \delta_n),$$

the interior disturbance is

$$R_2 = De^{\frac{1}{2n}\Psi_n \sin(2\sigma+\delta_n)\,.\,\eta}[\sin(n\eta - \sigma) + \ldots],$$

and the equations of continuity at the interface are, to a sufficient approximation,

$$A + B = -D\sin\sigma,$$

$$im(A - B) = Dn\cos\sigma,$$

whence

$$\frac{B}{A} = -e^{2i\arctan\frac{m}{n}\tan\sigma} \quad \ldots \quad (5{\cdot}6)$$

The interpretation of the symbolic expressions (5·5) and (5·6) for the ratio of the amplitudes of the reflected and incident waves readily follows. Taking the expression (5·5), we see that β is real so long as Ψ_0 is negative, or, since m^2 is essentially positive, so long as m^2 lies between 0 and $\left(\frac{pd}{\pi c}\right)^2(1 - K_0)$. This range of values of m for which β is real corresponds to glancing angles of incidence between 0 and $\arcsin\sqrt{1 - K_0}$; in it the modulus of $\frac{B}{A}$ is unity, so that the reflexion is perfect. Angles of incidence immediately outside this range correspond to small positive values of Ψ_0, so that β takes complex values; examination shows that the modulus of $\frac{B}{A}$ rapidly falls towards zero outside the range of perfect reflexion.

In the expression (5·6) we may, by (5·2), write n for m so long as Ψ_0 is near a squared integer n^2. The ratio of the reflected to the incident amplitude is therefore approximately $-e^{2i\sigma}$, the modulus of which is unity so long as σ is

real. Let ϕ be the glancing angle corresponding to

$$\sigma = \frac{\pi}{4} - \frac{\delta_n}{2},$$

so that from (5·3)

$$\sin^2\phi = 1 - K_0 + n^2\left(\frac{pd}{\pi c}\right)^2 \quad . \quad . \quad . \quad . \quad (5{\cdot}7)$$

In the neighbourhood of ϕ let $\theta = \phi + \epsilon$, where ϵ is small. Then (5·3) and (5·7) give

$$\epsilon = \frac{\Psi_n \lambda}{4nd\cos\phi}\cos(2\sigma + \delta_n).$$

We see, then, that so long as σ is real, θ is restricted to the range

$$\phi \pm \frac{\Psi_n \lambda}{4nd\cos\phi},$$

and that within this range the reflexion is perfect, but accompanied by a phase change.

For glancing angles outside this range $\cos(2\sigma + \delta_n)$ must be real and numerically greater than unity, so that σ is of the form

$$is - \frac{\delta_n}{2} \quad \text{or} \quad \frac{\pi}{2} + is - \frac{\delta_n}{2},$$

where s is real. The amplitude of reflexion has then the modulus e^{-2s}, which falls off very rapidly outside the range of perfect reflexion; at a distance from the edge equal to about half the width of the band the amplitude of reflexion has fallen to about 27 per cent. of totality. The amplitude of reflexion e^{-2s} may readily be expressed in terms of glancing angle $\phi + \epsilon$. If ϵ_1 denote the half-width of the range of perfect reflexion, the values of the amplitude appropriate to the three regions

$$\epsilon < -\epsilon_1, \qquad -\epsilon_1 < \epsilon < \epsilon_1, \qquad \epsilon > \epsilon_1$$

are respectively

$$-\frac{\epsilon + \sqrt{\epsilon^2 - \epsilon_1^2}}{\epsilon_1}, \qquad 1, \qquad \frac{\epsilon - \sqrt{\epsilon^2 - \epsilon_1^2}}{\epsilon_1}.$$

These are equivalent to the formulæ given by Darwin *.

The reflexion from the crystal is therefore negligible except over certain ranges of angles of incidence, in which there is perfect reflexion, and in the regions immediately

* C. G. Darwin, Phil. Mag. xxvii. p. 675 (1914).

bordering these ranges, in which the reflexion rapidly falls off to zero. The ranges of perfect reflexion are from 0 to $\arcsin\sqrt{1-K_0}$, and ranges of width $\frac{\Psi_n\lambda}{2nd\cos\phi}$ symmetrical about positions ϕ given by (5·7). The first of these regions may be regarded as arising by the total reflexion of the X-rays at the crystal face, while the others are the reflexions at the Bragg angles of spectra of the 1st, 2nd, ... nth order.

The value $\arcsin\sqrt{1-K_0}$ of the critical glancing angle shows that the crystal behaves, as regards total reflexion, like a homogeneous optical medium of refractive index $\sqrt{K_0}$. It will be observed that the nth order band of reflexion is symmetrical about a position given by (5·7), which differs slightly from the position

$$\phi_0 = \arcsin n\frac{\pi e}{pd}$$

given by Bragg's relation. If we denote $1-K_0$ by $2t$, we find

$$\phi-\phi_0 = t\sec\phi\operatorname{cosec}\phi,$$

which is the relation obtained by Darwin * on the assumption that Bragg's formula holds accurately within the crystal, but that owing to a refractive index less than unity by t, corresponding to a mean specific inductive capacity $1-2t$, the angle ϕ of incidence on the face of the medium is not the same as the angle of passage across the stratifications.

The range of perfect reflexion is in each case bordered by a region in which the reflexion falls off. Calculation shows that the region of perfect reflexion contributes to the area under the curve of intensity against glancing angle a constant fraction, equal to three quarters, of the whole.

Numerical estimates may be obtained by writing for the specific inductive capacity the Drude-Lorentz expression

$$K = 1-\frac{\rho e^2}{\pi m\nu^2},$$

where ν is the frequency $\left(=\frac{p}{2\pi}\right)$, and ρ the density of distribution of electrons. If ρ be expanded in a Fourier's series

$$\rho = \rho_0+\rho_1\cos 2\eta+\rho_2\cos 4\eta\ldots$$
$$+\rho_1'\sin 2\eta+\rho_2'\sin 4\eta\ldots,$$

* C. G. Darwin, Phil. Mag. xxvii. p. 315 (1914).

comparison with (2·3) gives the values

$$K_0 = 1 - \frac{4\pi e^2 c^2}{mp^2}\rho_0,$$

$$K_r = -\frac{4\pi e^2 c^2}{mp^2}\rho_r, \qquad K_r' = -\frac{4\pi e^2 c^2}{mp^2}\rho_r'.$$

For illustrative purposes we may take a medium in which the stratification of electron density is represented by only two terms of the series, so that

$$\rho = \rho_0 + \rho_1 \cos 2\eta.$$

Since ρ vanishes midway between the planes of greatest concentration, $\rho_1 = \rho_0 =$ mean density of electrons in the crystal. If we use as typical values

$$d = 2{\cdot}81 \times 10^{-8}, \qquad \frac{e}{m} = 5{\cdot}3 \times 10^{17},$$

$$\rho_1 = 6{\cdot}3 \times 10^{23}, \qquad e = 4{\cdot}77 \times 10^{-10},$$

$$c = 3 \times 10^{10},$$

we find that Ψ_1 is of the order of magnitude 10^{-5}, which justifies the rejection of Ψ_1^2 in comparison with Ψ_1. The breadth of the range of perfect reflexion in the first order of the platinum β radiation ($\lambda = 1{\cdot}11 \times 10^{-8}$ cm.) is about 3·7 seconds of arc, and at the centre of the range the radiation is damped to $\frac{1}{e}$ after traversing about 6000 atomic planes.

6. *Intensity of Reflexion from a Deep Crystal. The Polarization, Structure, and Temperature Factors.*

The widths of the reflexion ranges in the various orders are much too small to be directly observable, and in any actual experiment the finite size of the source and of the crystal would give rise to a complicated diffraction pattern. The intensity of reflexion of homogeneous radiation in any order, or "integrated reflexion" as usually observed, will, however, be proportional to the width of the range of perfect reflexion. Thus any cause which affects the intensity of reflexion must operate by altering this width, or, since the width in the nth order is proportional to Ψ_n, by altering Ψ_n.

The conclusion that the reflexion in any order is proportional to the corresponding harmonic term in the Fourier's series for the stratified reflecting power, which is equivalent to the present result, and which has an analogue in the theory

of the plane optical diffraction grating, was arrived at by Bragg *, whose investigation does not, however, exhibit the dependence of the reflexion on the width of the range over which it is perfect. In terms of the present analysis, the result rests on the peculiarity of the differential equation of the problem which was pointed out above, namely that its nth-order solution is determined chiefly by the nth-order coefficients in the expansion of K.

We may see in a general way how the width of the range of reflexion is governed by the fluctuation about a mean value of the specific inductive capacity, or, what comes to the same thing, by the reflecting power of the crystal planes, by using the principle that the resolving power of a diffracting system—that is, the narrowness of the range over which homogeneous radiation is reflected—is proportional to the number of diffracting elements. Since the radiation is rapidly damped in its passage through the medium at the proper angle by the operation of extinction, the deeper-lying strata are inoperative in determining the purity of the spectrum. The smaller the reflecting power of each layer, the greater will be the number of layers contributing to the whole reflexion, and the narrower the corresponding range of reflexion.

For radiation polarized perpendicular to the plane of incidence, the quantity $v=\gamma'/\surd\mathrm{K}$, where γ' is that part of the magnetic vector independent of t and x, was seen to satisfy the same equation (2·4) as R′, except that Ψ_n is now given by (2·6) instead of (2·5). An investigation similar to that of the preceding paragraph shows that the reflexion of v, and therefore of γ, is perfect over a range whose width is proportional to the new value of Ψ_n, and which is accordingly $1-\frac{2n^2}{\mathrm{K}_0}\left(\frac{\pi c}{pd}\right)^2$ times the width of the range of perfect reflexion of R. Thus the intensity of reflexion of the constituent of unpolarized radiation which is polarized perpendicular to the plane of incidence differs from the intensity of reflexion of the constituent polarized in the plane of incidence by the factor

$$\left|1-\frac{2n^2}{\mathrm{K}_0}\left(\frac{\pi c}{pd}\right)^2\right|,$$

which may be written, since

$$\frac{n^2}{\mathrm{K}_0}\left(\frac{\pi c}{pd}\right)^2 \doteqdot \sin^2\phi,$$

* W. H. Bragg, Phil. Trans. ccxv. A, p. 268 (1915).

as $|\cos 2\phi|$. The intensity of reflexion of unpolarized radiation is accordingly obtained from the expression for the intensity of reflexion of radiation polarized in the plane of incidence by multiplication by a factor

$$\tfrac{1}{2}(1+|\cos 2\phi|).$$

The structure factor expresses the reflexion from a crystal face the planes parallel to which are of two or more distinct types, alternating regularly, in terms of the reflexion from ideal crystals in which the planes are all of one type.

For simplicity we suppose that the variable part of the distribution of specific inductive capacity, or of negative electron density, may be regarded as the superposition of two parts, each of which is due to a different kind of atomic plane, and each of which is taken to be symmetrical, and expressed by

$$-\rho_1 \cos 2\eta - \rho_2 \cos 4\eta \ldots$$

and

$$-\rho_1' \cos 2(\eta-\delta) - \rho_2' \cos 4(\eta-\delta) \ldots,$$

so that $\frac{d\delta}{\pi}$ is the displacement of the one set of planes relative to the other. The variable part of the resultant specific inductive capacity throughout the crystal will be proportional to the sum of these two parts, that is, to

$$\Sigma(\rho_r+\rho_r' \cos 2r\delta)\cos 2r\eta + \Sigma\rho_r' \sin 2r\delta \sin 2r\eta,$$

and the intensity of reflexion will accordingly contain a factor

$$[(\rho_r+\rho_r' \cos 2r\delta)^2+(\rho_r' \sin 2r\delta)^2]^{\frac{1}{2}}$$
$$= [\rho_r^2+\rho_r'^2+2\rho_r\rho_r' \cos 2r\delta]^{\frac{1}{2}}.$$

If we assume that the shapes of the two constituent distributions are the same, that is, that $\frac{\rho_r}{\rho_r'}$ is independent of r and equal to the ratio $\frac{Z}{Z'}$ of the mean densities in the two types of planes, we obtain for the structure factor the usual expression

$$[Z^2+Z'^2+2ZZ' \cos 2r\delta]^{\frac{1}{2}}.$$

As a rough approximation it may be said that the effect of temperature is to cause the atoms to execute oscillations about their mean positions, and that the departures of their centres from the median plane at any instant follow the

usual distribution law; on this assumption a factor representing the influence of temperature vibrations on the intensity of reflexion may readily be deduced. Suppose that at the absolute zero the electron density corresponding to a series of atomic planes may be written as a cosine series

$$\rho_0+\rho_1\cos 2\frac{\pi y}{d}+\rho_2\cos 4\frac{\pi y}{d}\ldots.$$

When displaced a distance y' from the equilibrium position in a direction perpendicular to the plane, the atom giving rise to this distribution contributes to the electron density at $y=\mathrm{Y}$ an amount

$$\rho_0+\rho_1\cos\frac{2\pi}{d}(y'-\mathrm{Y})+\rho_2\cos\frac{4\pi}{d}(y'-\mathrm{Y})\ldots.$$

Now the relative number of atoms in any plane displaced through distances between y' and $y'+dy'$ is

$$\sqrt{\frac{\sigma}{2\pi k\mathrm{T}}}\,e^{-\frac{1}{2}\frac{\sigma y'^2}{k\mathrm{T}}}dy',$$

where $\frac{1}{2}\sigma$ is the potential energy for unit displacement, T the absolute temperature, and k is Boltzmann's constant, so that the density at $y=\mathrm{Y}$ is

$$\int_{-\infty}^{\infty}\sqrt{\frac{\sigma}{2\pi k\mathrm{T}}}\left(\rho_0+\rho_1\cos\frac{2\pi}{d}(y'-\mathrm{Y})\ldots\right)e^{-\frac{1}{2}\frac{\sigma y'^2}{k\mathrm{T}}}dy'$$

$$=\rho_0+\Sigma\rho_r e^{-\frac{2k\mathrm{T}}{\sigma}\frac{r^2\pi^2}{d^2}}\cos\frac{2r\pi\mathrm{Y}}{d}.$$

Hence the intensity of reflexion in the nth order is affected with the factor

$$e^{-\frac{2k\mathrm{T}}{\sigma}\cdot\frac{n^2\pi^2}{d^2}},$$

which is of the usual exponential form. But the assumptions on which this calculation is based are not refined enough for a comparison of the result with experiment.

The above analysis leads to values of the factors representing the influence on the intensity of reflexion of polarization, structure, and temperature, which are the square roots of the values obtained by a simpler theory in which each plane is assumed to scatter independently of the others. This result is in general agreement with Darwin's

later results, and with the more recent investigations of Ewald *.

In view of the short wave-length of X-rays, in comparison with which ordinary matter must be regarded as coarse-grained, it is remarkable that the crystal should be capable of being treated as a continuous optical medium. A suggested explanation is that when the radiation traverses the crystal in a direction near the reflecting angle, the portions of the incident wave-train which contribute to any wave-front of the reflected train are spaced out at intervals $2d \sin\theta = n\lambda$ behind each other, and therefore meet successive planes in the same phase, so that each reflected wave-front is made up of contributions coming from all the planes. This makes it possible to average out the irregularities of the individual planes over their whole number, or, in other words, to replace the discrete electronic structure of each plane by a continuous distribution.

I wish to express my indebtedness to Sir Joseph Larmor, at whose suggestion this investigation was undertaken.

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December 1925.

XCII. *On the Influence of Radiation on Ionization Equilibrium.* *By* MEGHNAD SAHA, *Physics Department, Allahabad University, and* RAMANI KANTA SUR, *Government Intermediate College, Allahabad, India* †.

1.

THE chief desideratum of the present theories of thermal ionization of gases is that they fail to take any account of the influence of radiation on ionization equilibrium. Yet it can easily be shown, and it has been pointed out by many investigators, that radiation plays an essential rôle in many physical and astrophysical phenomena. Russell ‡ pointed out the possible influence of radiation in the barium-sodium anomaly in the solar photosphere, where barium is found to be almost completely ionized, while sodium is only partially ionized, though both elements possess identical ionization potentials. He traced the phenomena to the fact that

* P. P. Ewald, *Phys. Ztschr.* xxvi. p. 29 (1924).
† Communicated by the Authors.
‡ Russell, Astrophysical Journal, lvi. May 1922.

Ba^+-atoms are susceptible to photospheric radiation, because the resonance lines lie at 4934, 4554, while Na^+-atoms are not so, because their resonance lines probably lie far in the ultra-violet. Milne* points out that radiation pouring out through the solar atmosphere is at a higher temperature than the atmosphere itself, and hence the observed ionization is at least partly due to radiation. In recent years, experiments † have been done in which comparatively cool vapours of alkalies have been ionized by ultra-violet radiation lying beyond the convergence frequency of the principal series of the element. In such cases, the ionization is a purely radiation effect. To the same class of phenomena belong the familiar absorption experiments of Wood and others, where vapours of metals are illuminated by continuous light. In this case the atoms are not ionized, but as a result of the interaction between matter and radiation the valency electron is lifted to higher orbits. There is, in fact, no essential difference between this class of phenomena and phenomena known as photo-chemical reactions, only in the latter case the unit mechanism of reaction is rather obscure.

The treatment of this class of phenomena from the theoretical side is fraught with several difficulties, viz. (1) the mechanism of absorption of a pulse of light by an atom has not yet been tackled successfully on the quantum-mechanical basis ; (2) in a reaction of this type, the reacting pulses do not all have the same frequency, *i. e.* the absorption lines have a finite breadth. This means that when pulses slightly differing from the resonance lines collide with the atom, there is a probability of their being absorbed, but the value of this probability factor varies from a maximum for the centre of the absorption line to rapidly decreasing values on both sides of the centre. Again, the maximum absorption varies from line to line. Thus Füchtbauer found that for the same intensity D_2 is twice as strongly absorbed as D_1.

Up to the present time neither the physical basis of fine width of absorption lines has been cleared up, nor are we in possession of any formula for absorption applicable to all the lines of a series.

2.

The attempts which have been made to deal with the interaction between matter and radiation ‡ may be broadly

* Milne, in a note to 'Nature,' see Month. Notices R. A. S. June 1925.

† Foote & Mohler, Physical Review, xxvi. p. 195 (1925).

‡ See Month. Notices R. A. S. lxxxv. June 1925; the controversy between Milne and Stewart.

subdivided into two classes—(1) those based on the methods used in the kinetic theory of gases; (2) those based on thermodynamical methods. To the first category belong the works of Milne * "On the Statistical Equilibrium in relation to Photoelectric Effect," and of R. H. Fowler † "On Statistical Equilibrium and the Mechanism of Ionization by Electronic Impacts." In these cases some knowledge or some assumption regarding the details of the unit mechanism of reaction is essential. Milne assumes that high temperature ionization is largely a volume photoelectric phenomenon, while Fowler treats the case where ionization is promoted by collision, in particular by electronic impacts. It may be mentioned that these methods follow on the lines initiated by Guldberg and Waage, Boltzmann, and J. J. Thomson in dealing with the problems of dissociation equilibrium and molecular aggregation ‡. In the thermodynamical method, as developed by van't Hoff, Nernst, Sackur §, and others, a knowledge of the detailed mechanism is not so indispensable.

The result is obtained by a treatment of the initial and final states, provided the net charge in energy-content is known. The theory thereby loses somewhat in definiteness, but it has the compensating advantage of being free from the vagueness of the assumptions involved in the kinetic methods.

In the present paper we have followed Ehrenfest's method of dealing with dissociation equilibrium. Attempts in this direction have already been made by R. H. Fowler ‖, Fowler and Milne ¶, and by Becker **. But they confined their attention to the production of metastable states.

Ehrenfest †† has shown that the behaviour of a mixture of gases in thermodynamical equilibrium can be defined by a function $\{\gamma\}$ which may be regarded as the total phase-space described by the system. The function $\{\gamma\}$ is allied to the familiar entropy function, but Ehrenfest did not trace the connexion between the two. In two previous papers ‡‡, we have shown that $\{\gamma\}$ is connected with Boltzmann's

* Milne, Phil. Mag. (6) xlvii. p. 209.
† R. H. Fowler, Phil. Mag. (6) xlvii. p. 257.
‡ For a summary, see Jeans, 'Dynamical Theory of Gases,' chap. 7, pp. 209–219.
§ See Sackur, 'Thermodynamics,' chap. 9.
‖ Fowler, Phil. Mag. (6) xlv. p. 1.
¶ Fowler & Milne, Month. Notices Roy. Ast. Soc. lxxxiii. p. 403.
** Becker, *Zs. für Physik*, xviii. p. 325.
†† Ehrenfest & Trkal, *Proc. Amst.* xxi. (1920); *Ann. der Physik*, lxiii.
‡‡ Saha & Sur, Phil. Mag. Jan. 1926, p. 279.

probability function W, by the relation :

$$W = \{\gamma\}/\{\gamma\}_0,$$

where $\{\gamma\}_0$ = value of $\{\gamma\}$ when the system is reduced to absolute zero of temperature.

This theorem holds not only for matter, but we showed in the second paper that it also holds for radiation. The entropy of radiation can be calculated from formula (1) by an extension of S. N. Bose's method *.

This is equivalent to treating radiation as a new com ponent in chemical equilibrium. A similar view has already been expressed by Smit ; according to him the familiar phase-rule

$$F = C + 2 - P$$

has to be replaced in photochemical reactions by the rule $C + 3 - P$. The photochemically active light plays the rôle of a new component.

Turning to the present case, it is easy to see that a sodium atom with its electron in the $2p$-orbits or any higher orbit may be regarded as a chemical entity different from a normal Na-atom. The Na_{2p} atom may, for practical purposes, be regarded as compound of Na- (normal) and D_1, D_2 pulses. Thus the lines of the sodium spectrum, Na^+-ion, and the electron may be regarded as the independent components out of which the whole system, consisting of normal atom Na^+ and the metastable states of Na, are evolved.

3.

Let us now consider a system consisting of

n_1 ..... neutral atoms,

n_2 ..... ionized atoms,

n_3 ..... free electrons.

Let $n_1 + n_2 + n_3 = n$, and K = kinetic energy of the material particles. Let $N_s\,d\nu$ = total number of quanta of frequency ν comprised within the range $d\nu$. Then, according to the methods described in the previous papers,

$$W_{d\nu} \text{ for radiation} = \Pi \left\{ \frac{(A_s + N_s)!}{A_s!\, N_s!} \right\}^{d\nu} \quad . \quad . \quad (1)$$

* S. N. Bose, *Zs. für Physik*, xxvi. p. 178 (1924); xxvii. p. 384.

For the material particles

$$W_p = \frac{{\mu_1}^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{{\mu_2}^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{{\mu_3}^{n_3}}{h^{3n_3} \cdot n_3!} \cdot \quad . \quad . \quad (2)$$

We shall here ignore the motion of an electron about its nucleus, and suppose that each material particle has only three degrees of freedom, viz. those corresponding to the motion of translation along three mutually perpendicular axes. Therefore, we have,

$$\left.\begin{aligned} \mu_1 &= \int \ldots dx\, dy\, dz \cdot dp_x\, dp_y\, dp_z \\ &= V \int \ldots dp_x\, dp_y\, dp_z, \\ \mu_2 &= V \int \ldots dp_x'\, dp_y'\, dp_z', \\ \mu_3 &= V \int \ldots dp_x''\, dp_y''\, dp_z'', \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

V = total volume of the gas, and p_x, p_y, p_z, etc. represent the momenta coordinates of the particles.

Hence

$$W_p = \frac{V^n}{h^{3n}} \frac{1}{n_1!\, n_2!\, n_3!} \int \ldots dp_{1x}\, dp_{1y}\, dp_{1z} \ldots dp_{1x}'\, dp_{1y}'\, dp_{1z}' \ldots dp_{1x}''\, dp_{1y}''\, dp_{1z}'',$$

the integrals being taken for all molecules of each class. The total kinetic energy K being given, the integration is to be performed subject to the condition

$$\sum^{n_1} \frac{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}{2M} + \sum^{n_2} \frac{p_{1x}'^2 + p_{1y}'^2 + p_{1z}'^2}{2M} + \sum^{n_3} \frac{p_{1x}''^2 + p_{1y}''^2 + p_{1z}''^2}{2m} = K, \quad . \quad (4)$$

where M = mass of a neutral atom and m = mass of an electron.

Thus

$$W_p = \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1!\, n_2!\, n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left|\left(\frac{3n}{2}\right)\right.} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3}. \quad . \quad . \quad . \quad (5)$$

For the total system, consisting of radiation and the material particles,

$$W = W_{d\nu} \cdot W_p,$$

or

$$W = \Pi \left\{ \frac{(A_s + N_s)!}{A_s!\, N_s!} \right\}^{d\nu} \cdot \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1!\, n_2!\, n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left|\left(\frac{3n}{2}\right)\right.} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3}. \quad (6)$$

Let us now consider a unit process in which a neutral atom is dissociated into a free electron and a positively charged atom by the absorption of a quantum $h\nu$. Then

n_1	changes to	$n_1 - 1$
n_2	,,	,, $n_2 + 1$
n_3	,,	,, $n_3 + 1$
n	,,	,, $n + 1$
$N_s\, d\nu$	,,	,, $N_s\, d\nu - 1$.

The total energy E of the combined system, however, remains unaltered, *i. e.* $dE = 0$,

$$dE = dK + \chi - h\nu_3 = 0,$$

or

$$dK = h\nu - \chi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where χ represents the ionization potential per atom. The probability of the system now is

$$W' = \Pi \frac{(A_s\, d\nu + N_s\, d\nu - 1)!}{A_s\, d\nu!\, (N_s\, d\nu - 1)!} \cdot \frac{V^{n+1}}{h^{3(n+1)}} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{(n_1 - 1)!\, (n_2 + 1)!\, (n_3 + 1)!} \cdot \frac{(\sqrt{M^3})^{n_1 - 1} (\sqrt{M^3})^{n_2 + 1} (\sqrt{m^3})^{n_3 + 1}}{\left|\frac{3(n+1)}{2}\right.}. \quad (8)$$

For equilibrium,

$$dW = W' - W = 0, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

whence we obtain,

$$\frac{1}{n_1} \cdot \frac{A_s\, d\nu + N_s\, d\nu}{N_s\, d\nu} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left|\left(\frac{3n}{2}\right)\right.} = \frac{V}{h^3} \cdot \frac{1}{n_2 n_3} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{\left|\left(\frac{3(n+1)}{2}\right)\right.} \cdot m^{3/2}. \quad . \quad (10)$$

Replacing $\left|\overline{\frac{(3n)}{2}}\right.$ by $\left(\frac{3n}{2}\right)!$ and using Stirling's formula,

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{\frac{3n}{2}} \right\}^{3/2} \cdot \left(1 + \frac{dK}{K}\right)^{\frac{3n}{2}},$$

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{\frac{3n}{2}} \right\}^{3/2} \cdot \left(1 + \frac{3n}{2}\frac{dK}{K}\right). \quad (11)$$

Putting $K = \frac{3n}{2} kT$, and using (7), we have, after taking logarithms,

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{h\nu - \chi}{kT} + \log \left\{ \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot (2\pi m k T)^{3/2} \right\}. \quad (12)$$

Now

$$\frac{N_s}{A_s + N_s} = \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Using partial pressures, we have, after some reduction,

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{Nh\nu - U}{RT} + \log \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}, \quad . \quad (14)$$

where N = Avogadro number,

U = Ionization potential for a mol.

If the temperature of radiation be the same as that of the gaseous system

$$\rho_\nu = 8\pi \frac{h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \quad . \quad . \quad . \quad . \quad (15)$$

the quantity $\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}$ reduces to $e^{-\frac{h\nu}{kT}}$, and the equation (14) reduces to the familiar form

$$\log \frac{p_2 \cdot p_3}{p_1} = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad (16)$$

If, within the reaction-space, the density of radiation be the same as that given within black-body chamber,

$$\frac{\rho_\nu}{8\pi\frac{h\nu^3}{c^3}+\rho_\nu} = e^{-\frac{h\nu_s}{kT_s}},$$

where T_s = temperature of radiation.

Then

$$\log\frac{p_2\cdot p_3}{p_1} = \frac{N h\nu}{RT}\left(\frac{1}{T}-\frac{1}{T_s}\right) - \frac{U}{RT} + \tfrac{5}{2}\log T + \log\left\{\frac{(2\pi m)^{3/2}\cdot k^{5/2}}{h^3}\right\}. \quad (17)$$

This formula is practically identical with one given earlier by Einstein *. Einstein's formula was deduced for photochemical reactions, and runs thus :

$$\log\frac{n_2\cdot n_3}{n_1} = \frac{N h\nu}{R}\left(\frac{1}{T}-\frac{1}{T_s}\right) + \frac{1}{R}\Sigma\,\delta n\left\{c_v\log T + c_1 - (c_v+R) - \frac{b_1}{T}\right\}. \quad (17')$$

It is easy to see that we can apply this formula directly to the present case and arrive at (17).

Formula (14) is, however, quite general and can be adapted to the circumstances of the case. In place of ρ_ν, we have now to use I_ν, where I_ν is the intensity of light from the source in the reaction-space. The formula then takes the form :

$$\log\frac{p_2\cdot p_3}{p_1} = \frac{N h\nu - U}{RT} + \log\frac{I_\nu}{2\frac{h\nu^3}{c^2}+I_\nu} + \tfrac{5}{2}\log T + \log\left\{\frac{(2\pi m)^{3/2}\cdot k^{5/2}}{h^3}\right\}. \quad (18)$$

As a special case, let the radiation proceed from a black-body radiator at temperature T_s, and let the radiation be confined within a solid angle w. Let F_ν be its residual intensity in the reaction-space, *i. e.* $F_\nu = r\cdot I_\nu$, r being a fraction and

$$I_\nu = 2\frac{h\nu^3}{c^2}\cdot\frac{1}{e^{\frac{h\nu}{kT_s}}-1}.$$

* Einstein, *Ann. der Physik*, xxxvii. p. 838.

The quantity $\frac{\rho_\nu}{8\pi\frac{h\nu^3}{c^3}+\rho_\nu}$ is to be replaced by $\frac{r\frac{w}{4\pi}\cdot \mathrm{I}_\nu}{2\frac{h\nu^3}{c^2}+r\frac{w}{4\pi}\mathrm{I}_\nu}$,

or to a first approximation by $r\frac{w}{4\pi}e^{-\frac{h\nu}{k\mathrm{T}_s}}$.

The formula (14) then reduces to

$$\log\frac{p_2\cdot p_3}{p_1}=\frac{\mathrm{N}h\nu-\mathrm{U}}{\mathrm{RT}}+\log\left(r\frac{w}{4\pi}e^{-\frac{h\nu}{k\mathrm{T}_s}}\right)+\tfrac{5}{2}\log\mathrm{T}$$
$$+\log\left\{\frac{(2\pi m)^{3/2}\cdot k^{5/2}}{h^3}\right\}. \quad (18')$$

4.

Influence of Radiation in producing Higher Quantum States.

By a similar treatment it is possible to deduce the equilibrium between normal and excited states. Let

n_1 = number of atoms in the normal state (1*s* in the case of Na, 2*p* in the case of Al).

n_2 = number in any higher excited state (2*p* in the case of Na).

$n_1+n_2=n$.

$\mathrm{N}d\nu$ = number of energy pulses within the frequency region ν, $\nu+d\nu$. The normal atoms pass to the excited state by the absorption of these pulses.

Then we have

$$\mathrm{W}=\left\{\frac{(\mathrm{A}+\mathrm{N})!}{\mathrm{A}!\,\mathrm{N}!}\right\}^{d\nu}\cdot\frac{{g_1}^{n_1}}{h^{3n_1}\cdot n_1!}\cdot\frac{{g_2}^{n_2}}{h^{3n_2}\cdot n_2!}$$
$$\cdot\frac{\mathrm{V}^n}{\left|\left(\frac{3n}{2}\right)\right.}\cdot(2\pi\mathrm{K})^{\frac{3n}{2}}\cdot m^{\frac{3n}{2}};$$

g_1 and g_2 represent the statistical weights of the two states, K the total kinetic energy, and m the mass of the atoms.

If we take a virtual displacement (unit change) in which n_1 changes to n_1-1, n_2 to n_2+1, and $\mathrm{N}d\nu$ to $\mathrm{N}d\nu-1$, we have

$$\mathrm{W}'=\frac{(\mathrm{A}d\nu+\mathrm{N}d\nu-1)!}{\mathrm{A}d\nu!\,(\mathrm{N}d\nu-1)!}\cdot\frac{{g_1}^{n_1-1}\cdot{g_2}^{n_2+1}}{h^{3n}\cdot(n_1-1)!\,(n_2+1)!}$$
$$\cdot\frac{\mathrm{V}^n}{\left|\left(\frac{3n}{2}\right)\right.}\cdot\{2\pi(\mathrm{K}+d\mathrm{K})\}^{\frac{3n}{2}}\cdot m^{\frac{3n}{2}},$$

where $d\mathrm{K}=h\nu-\chi$; χ now represents the difference in the energy levels of the two states.

Now putting

$$\mathrm{W}'-\mathrm{W}=0 \quad \text{and} \quad \mathrm{K}=\frac{3n}{2}k\mathrm{T},$$

we have

$$\frac{n_2}{n_1}=\frac{g_2}{g_1}\cdot\frac{\mathrm{N}}{\mathrm{A}+\mathrm{N}}\cdot\left(1+\frac{h\nu-\chi}{k\mathrm{T}}\right),$$

or

$$\frac{n_2}{n_1}=\frac{g_2}{g_1}\cdot\frac{\mathrm{N}}{\mathrm{A}+\mathrm{N}}\cdot e^{\frac{h\nu-\chi}{k\mathrm{T}}} \quad \text{to an approximation,}$$

i. e.

$$\frac{n_2}{n_1}=\frac{g_2}{g_1}\cdot\frac{\rho_\nu}{8\pi\frac{h\nu^3}{c^3}+\rho_\nu}\cdot e^{\frac{h\nu-\chi}{k\mathrm{T}}} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

When the radiation is in temperature equilibrium with the gas, it is easy to see that

$$\frac{n_2}{n_1}=\frac{g_2}{g_1}\cdot e^{-\frac{\chi}{k\mathrm{T}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

When T is sufficiently high

$$\frac{n_2}{n_1}=\frac{g_2}{g_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

as is apparent from the definition of weight factor.

Conclusion.

It will be seen from an inspection of the formulæ deduced that the finite breadth of the absorption band does not occur in any one of them. This shows that the formulæ can be regarded only as approximate. This is not unexpected, because the idea of absorption is rather foreign to the thermodynamical methods.

After a short note announcing this result was published in 'Nature' (Nature, April 11, 1923), Woltjer published a note in which he mentioned that the formulæ (14) and (19) could be obtained from Milne's method of treatment. We have found that this method gives identical results. But, contrary to our expectations, even in this method of treatment the absorption factor does not occur.

October 1, 1925.

XCIII. *The Dielectric Constants of Benzene Solutions.* *By* Prof. J. R. Partington, *D.Sc.*, *and* J. F. J. Rule, *B.Sc.**

THE dielectric constants of solutions of solids in non-ionizing solvents appear to have been little investigated, although those of several liquid mixtures have been determined (*e.g.*, by Philip, *Z. phys. Chem.* xxiv. p. 18, 1897; and Lange, *Z. Physik*, xxxiii. p. 169, 1925). Walden and his co-workers have investigated several conducting solutions (Walden, *Bull. Acad. St. Petersb.* vi. pp. 305 and 1055, 1912; J. Am. Chem. Soc. xxxv. p. 1649, 1913; Walden, Ulich and Werner, *Z. phys. Chem.* cxvi. p. 261, 1925; Ulich, *Z. Electrochem.* xxxi. p. 413, 1925).

In the present research, the dielectric constants of solutions of *m*-dinitrobenzene, phenol, and benzoic acid in benzene have been determined by the Nernst method (*Z. phys. Chem.* xiv. p. 622, 1894) as modified by Turner (*ibid.*, xxxv. p. 385, 1900).

It was found in the cases of *m*-dinitrobenzene and phenol that the dielectric constant of the solutions increased directly with concentration and seemed to approach the value of the pure solute in the *fused* state. Thus *m*-dinitrobenzene was found by Augustin (Diss. Leipzig, 1893) to have a dielectric constant of 2·85 when solid and 20·65 when fused at 90° C., whilst that of phenol when fused at 48° C. is 9·68 (Drude, *Z. phys. Chem.* xxiii. p. 267, 1897). The values extrapolated from our results are 30·5 for *m*-dinitrobenzene at 20° C., and 13·8 for phenol at 18° C. The curve for *m*-dinitrobenzene appears to decrease its gradient towards the higher concentrations, but the limitation of solubility would not allow of further investigation of the curve.

With benzoic acid the dielectric constant increased with concentration to a maximum and then decreased. No determination of the dielectric constants of benzoic acid appear to have been made. We have made a determination for solid benzoic acid by melting it in the dielectric trough and allowing it to crystallize, and found the value 1·7.

The trough in which the solutions were contained (Nernst, Turner, *loc. cit.*) was of brass and was at first nickel plated. It was found, however, that the benzoic acid solutions attacked the nickel slowly and the solution became green. This was overcome by well plating the trough with silver.

* Communicated by the Authors.

The conductivity of the solutions was inappreciable, being no greater than that of benzene except in the case of phenol solutions at the higher concentrations.

The apparatus was calibrated by using benzene as a standard, the value of the dielectric constant of benzene being taken as 2·288 at 18° C (Turner, *loc. cit.*), which is the usually accepted value. Modern determinations of the dielectric constant of benzene, however, seem to point to a value of 2·24 (Sayce and Briscoe, J. Chem. Soc. cxxvii. p. 315, 1925, and Harris, *ibid.* cxxvii. p. 1049, 1925), but for the present the older value is retained.

Materials.

Benzene.—Pure thiophen-free benzene of Kahlbaum was carefully dried over sodium and fractionally distilled. B.Pt.=80°·5 C. $D_4^{20}=0·8779$.

m-dinitrobenzene prepared from benzene and nitric acid was crystallized twice from alcohol. M.Pt.=80°·8 C.

Phenol.—British Drug Houses crystals which were used were found to be of good purity. They were distilled and the end portion rejected. M.Pt.=40°·7 C. (M.Pt. of very pure phenol is 41°·5 C., Stratton and Partington, Phil. Mag. xliii. p. 436, 1922).

Benzoic Acid.—Pure chlorine-free acid was twice crystallized from water, dried, and then sublimed. M.Pt.=121°·4 C.

Results.

TABLE I.

m-dinitrobenzene in benzene. Temp.=20° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0	0	2·286
0·088	1·66	2·82
0·176	3·31	3·34
0·264	5·05	3·95
0·351	6·55	4·24
0·423	7·55	4·68
0·562	9·83	5·57
0·628	11·19	5·91
0·742	12·95	6·51
0·842	14·44	7·22
1·007	16·62	7·59

Fig. 1—*m*-Dinitrobenzene in Benzene.

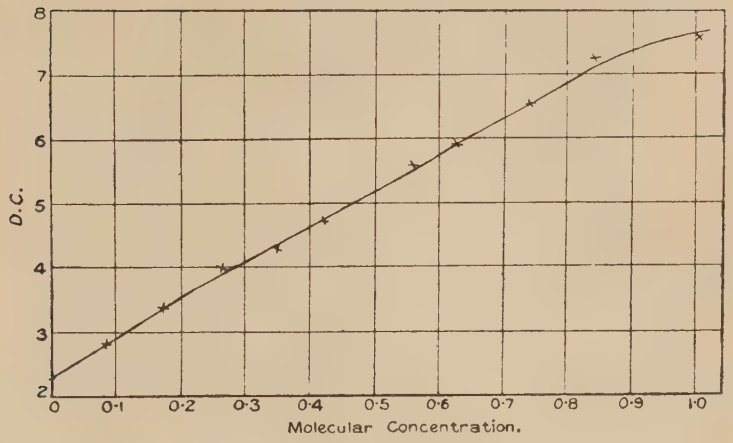


TABLE II.

Phenol in benzene. Temp. = 18° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0·00	0·00	2·288
0·700	7·73	2·64
0·951	12·48	2·80
1·40	15·23	3·08
1·90	19·66	3·37
2·82	26·61	4·02
3·85	33·14	4·62
5·57	41·34	5·61
6·55	45·74	6·25

Fig. 2.—Phenol in Benzene.

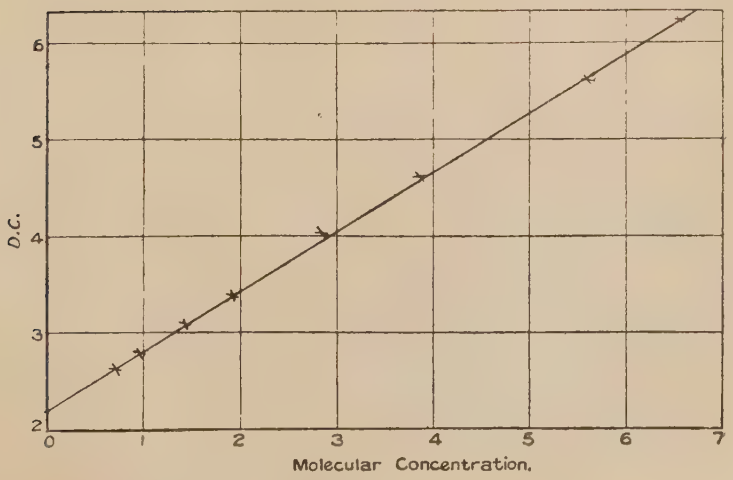
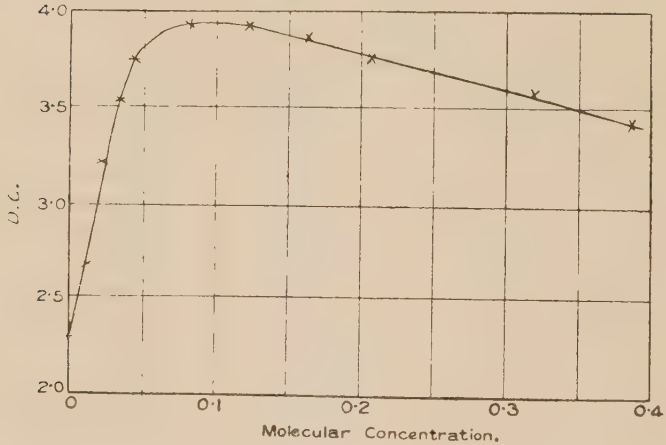


TABLE III.

Benzoic Acid in benzene. Temp.=18° C.

Molec. Conc.	Per cent. Conc. by weight.	D.C.
0	0	2·288
0·011	0·15	2·67
0·023	0·30	3·22
0·035	0·46	3·53
0·046	0·61	3·76
0·082	1·11	3·94
0·123	1·69	3·93
0·164	2·24	3·87
0·205	2·81	3·74
0·322	4·44	3·57
0·393	5·38	3·43

Fig. 3.—Benzoic Acid in Benzene.



Summary.

1. The dielectric constants of solutions of *m*-dinitrobenzene, phenol, and benzoic acid in benzene were determined.

2. In the cases of *m*-dinitrobenzene and phenol the dielectric constant increased steadily with concentration and appeared to approach the value for the pure solute in the fused state.

3. In the case of benzoic acid, the dielectric constant increased with concentration to a maximum and then decreased.

We wish to acknowledge the receipt of a Research Grant from the Chemical Society to one of the authors (J.F.J.R.), which has defrayed part of the cost of the investigation.

The work is being extended to conducting solutions.

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XCIV. *Lines of Maximum Principal Stress in Thin Mild Steel Plates of Rectangular Shape fixed along the Edges and uniformly loaded.* *By* B. C. Laws, *D.Sc., A.R.C.Sc., M.I.C.E., and* A. O. Allen, *M.A., B.Sc., A.R.C.Sc.**

STRESS distribution in thin disks fixed at their boundaries is not easy of determination—at least where the boundaries suffer abrupt changes in direction—whether the problem is approached from pure mathematical considerations or by the aid of experiment.

Both processes involve much labour. In the former certain assumptions may be made to facilitate the solution, but the results obtained are more or less unsatisfactory. Experimental investigation, however, provides data which under careful mathematical analysis produce results to which little objection can be raised.

The problem is not only of academic interest, but is commonly met with in certain classes of constructive engineering, and from both points of view the solution is of value.

Experiments were carried out in the Physics Department of the University of Leeds during the latter part of the war, and subsequently, upon rectangular-shaped plates of different thicknesses and dimensions fixed at their boundaries and subject to uniformly distributed loads.

An important part of the inquiry was to determine the value and position of "maximum stress," a knowledge of which has a very important bearing on certain practical problems. It formed the subject of a paper † by one of the authors, recently published, in which formulæ were obtained giving "maximum stress" and "maximum deflexion" in terms of the dimensions of the plate, its thickness, and the load imposed.

The inquiry is now carried a little further, and it has been sought to determine in what manner the stress varies from point to point and how the plate changes in form under the

* Communicated by the Authors.

† Proceedings of the Institution of Civil Engineers, vol. ccxiii. part 1.

load. Several points of physical significance arise out of the analysis, and certain characteristics become evident which without the aid of experimental data can only be a matter of conjecture.

Microscopic observations of deflexions were made at the points of intersection of ordinates drawn on the plate surface parallel to the sides of the rectangle, and represented graphically. The first and second derived curves of the graphs were calculated by the "method of differences."

A check was placed on the curves of slope by observing the change of gradient of the plate by means of small mirrors mounted on a suitable table geometrically supported at the several points of observation and confirmed the near accuracy of the calculations.

The analysis was based on the following theoretical principles :—

If $z=f(x, y)$ be the equation of the plate surface after deflexion referred to a datum plane situated midway between the initial plate surfaces, then the radii of principal curvature at (x, y, z) are respectively given by

$$\rho=\frac{t+r\pm\sqrt{(r-t)^2+4s^2}}{2(s^2-r\,.\,t)},$$

where

$$t=\frac{d^2z}{dy^2},\quad r=\frac{d^2z}{dx^2},\quad \text{and}\quad s=\frac{d^2z}{dx\,.\,dy},$$

the plate surface being assumed of small curvature.

The principal stresses due to bending have been calculated from the formulæ :

$$p_1=\frac{\sigma\,.\,\mathrm{E}\,.\,\mathrm{T}}{2(\sigma^2-1)}\left(\frac{1}{\rho_2}+\frac{\sigma}{\rho_1}\right),\quad \text{and}\quad p_2=\frac{\sigma\,.\,\mathrm{E}\,.\,\mathrm{T}}{2(\sigma^2-1)}\left(\frac{1}{\rho_1}+\frac{\sigma}{\rho_2}\right),$$

where ρ_1 and ρ_2 are the principal radii of curvature given above, $\frac{1}{\sigma}$ = Poisson's ratio, E = Young's modulus, and T = the thickness of the plate.

The values of E, and Poisson's ratio, were determined by separate experiments on samples cut from the plates, and T by weighing the plates.

r, s, and t were obtained by differentiating twice the deflexion graphs represented by

$$z=a+\frac{x}{h}\,.\,d_1+\frac{x}{h}\left(\frac{x}{h}-1\right)\frac{d_2}{2!}+\frac{x}{h}\left(\frac{x}{h}-1\right)\left(\frac{x}{h}-2\right)\frac{d_3}{3!}+\ldots.$$

and $z=a+\frac{y}{h}d_1+$ etc.,

in which the ordinates of the curve at any section are equally spaced at intervals "h"; "a" is the first term of a series of consecutive ordinates, d_1 d_2 d_3 .... the first terms of the successive order of differences of the ordinates, and x (or y) the abscissa value of any—the nth—ordinate z whereof x (or y) $= (n-1)h$.

By the aid of the foregoing principles the variation of stress along the several sections was graphically represented to a suitable scale, and the graphs cut by lines (or planes) parallel to the initial plate surface at a height from the latter representing certain stress values, the intersections being then projected on to the plate surface and the loci of particular stress values obtained. The latter are shown in the accompanying diagram.

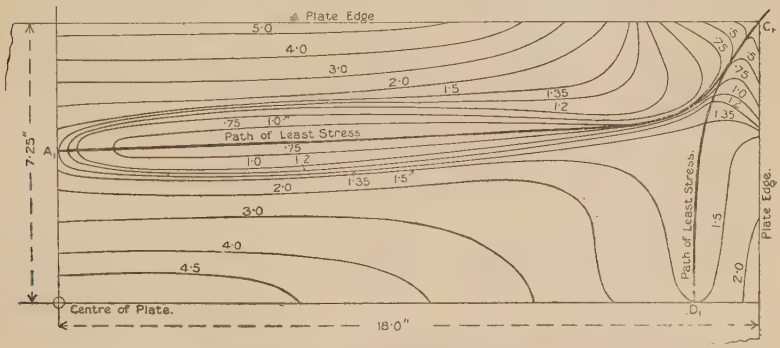


Diagram of "Lines of Maximum Principal Stress" for a thin mild steel plate 36 in. × 14·5 in. × ·244 in. thickness, fixed along its edges and subject to a load of ·0045 ton per sq. inch of surface.
Particular stress values in tons per sq. inch are indicated by numerals in the diagram.

The stress reaches a maximum at the middle point of the longer edges of the rectangle; it falls off slowly along the edge for a distance of about half its length and then quickly diminishes towards the corners of the rectangle where it approaches zero.

Along the axis through the centre of the plate parallel to the shorter side of the rectangle the stress diminishes to a comparatively small value at a distance from the plate centre depending upon the ratio between the sides of the rectangle, increasing again to a value at the centre of the plate less than that at the middle point of the longer side.

There is a similar variation along the shorter side and longer axis of the rectangle, but here the stress values generally are not so great.

The path pursued by a "particular stress value" is indicated in the diagram, an examination of which shows that the "lines of constant stress" follow each other in a very orderly manner.

The diagram refers to a plate 36 in. × 14·5 in. of thickness ·244 inch, and subject to a hydrostatic load of ·0045 ton per square inch of surface.

The thick lines A_1C_1, D_1C_1 in the diagram—drawn through the points of least stress in the several sections—may be termed the "path of least stress" for the plate. They correspond to nodal lines in a vibrating plate, and mark the demarcation between those portions of the plate, having opposite curvature, whereof the portions enclosed between them and the sides of the rectangle are of like curvature and opposite in sign to that of the area which they enclose in the body of the plate.

Had the plate been fixed independently along two parallel edges only so that the remaining edges are free, the path of least stress would obviously have been parallel to the former and correspond to the position of contraflexure in a simple beam fixed at its ends.

January 21, 1926.

XCV. *The Adsorption of Gases by Activated Charcoal at Very Low Pressures.*—II. *At* −183° *C. By* H. Rowe, *B.Sc., Demonstrator in Physics, University College of the South-West of England, Exeter* *.

1. Introduction.

In previous experiments † the author has determined the quantitative adsorption of various gases by activated coconut charcoal at low pressures and 20° C., and it was shown from these results that the adsorption isotherm is better represented by an equation of the type

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha \quad . \quad . \quad . \quad . \quad . \quad (1)$$

than by the equation which is usually quoted, viz.

$$\alpha = kP^{\frac{1}{n}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α = number of c.c., at N.T.P., adsorbed per gram of charcoal;

P = pressure in cm. of mercury;

A_0, A_1, k, and $\frac{1}{n}$ are constants depending on the particular gas.

* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S.

† Phil. Mag. li. p. 109 (1926).

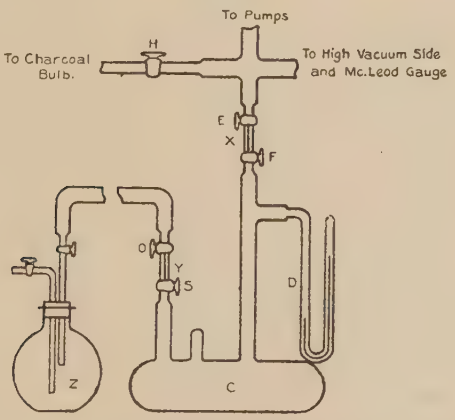
It was found that at very low pressures the isotherm was not tangential to the volume axis, as is to be expected from a mathematical analysis of equation (2), but the tangent of the isotherm was of the same order of magnitude as that calculated from equation (1). Further, the relationship between α and P was not linear except below pressures of the order 10^{-3} mm., and in general the absolute value of this pressure varies with the boiling-point of the gas ; it decreases as the boiling-point increases.

It is well known that a lowering in the temperature of charcoal causes a very great increase in its adsorptive capacity, and measurements made at very low temperatures are more reliable than those made at air temperatures, because in the latter case only small quantities are adsorbed. The experiments previously described have therefore been carried to a further stage by determining the quantities of nitrogen, hydrogen, and carbon monoxide adsorbed when the activated coconut charcoal is maintained at $-183°$ C. by immersion of its containing-bulb in liquid oxygen.

2. Experimental Arrangement.

The apparatus used was similar to that employed previously, and the experimental procedure was similar except

Fig. 1.



for the method of introducing quantities of gas into the high vacuum side. It was found that admitting small volumes of gas by alternately opening and closing the taps F and E, measuring the pressure p_1 in the high vacuum side, then admitting the gas to the charcoal and noting the final pressure p_2, practically all the gas was adsorbed, and no

appreciable increase in the equilibrium pressure within the limits of error of the experiment could be detected, Accordingly a modified method was adopted. The reservoir C was charged with gas from the containing-bulb Z, and its pressure read on the manometer D. Gas was then admitted to the high vacuum side, the tap H being closed, until the pressure in D fell to a desired level; the taps between C and the high vacuum side were then closed and the pressure in D read after it had become steady. From a knowledge of these pressures and the component volumes the new pressure in the high vacuum side could be calculated thus :—

Let

p_1' = original pressure in C in mm.;

p_2' = final " " "

p_2 = original pressure in high vacuum side;

p_1 = final " " " "

V = volume of high vacuum side;

v = volume of C.

Then $$p_1 = \frac{v(p_1'-p_2')}{V} + p_2;$$

V = 3163 c.c.; v = 128·5 c.c.;

$p_1'-p_2'$ = approx. 100 mm. of mercury;

p_1 was therefore of the order of 4 mm.

The quantities of gas adsorbed were so large that it was found convenient to calculate them in c.c. at N.T.P.

Let

p_1 = original pressure in high vacuum side;

p_2 = final " " " "
after adsorption had taken place;

θ = temperature in ° C.;

m = mass of charcoal in grams.

Then the quantity adsorbed per gram of charcoal in c.c. at N.T.P. is given by

$$\alpha = \frac{V(p_1-p_2).273}{m.760.(273+\theta)}.$$

As in the previous experiments, it is assumed that the total quantity of gas, α, in the charcoal at any given equilibrium pressure p is the sum of all the quantities adsorbed.

The equilibrium pressure p will not be equal to the final pressure p_2 in the high vacuum part, as a correction must be applied for thermal diffusion; the charcoal, and the gas immediately surrounding it, is at a much lower temperature than the remainder of the apparatus. The equilibrium pressure at $\theta°$ C. is given by

$$p = p_2\sqrt{\frac{90}{273+\theta}}.$$

The temperature of liquid oxygen is taken as $-183°$ C.

The same sample of charcoal was used for nitrogen, hydrogen, and carbon monoxide, but as it was suspected that the presence of the other gases affected the adsorptive capacity of the charcoal for hydrogen, a fresh sample of reactivated charcoal was used with this gas. In actual practice it was found that this fresh sample had a far larger adsorptive capacity for hydrogen than the one that had been used in the previous case.

3. Experimental Results.

a. *Nitrogen.*

The nitrogen used in these experiments was prepared by a method suggested by Waran *. When dilute ammonia is acted upon by bromine water, the resulting nitrogen is free from all impurities except water-vapour; this was removed by passing the gas over phosphorus pentoxide, and the bulb in which the gas was stored also contained a layer of phosphorus pentoxide.

In the initial adsorption, *i. e.* until the final pressure had reached the order of 5×10^{-4} mm., gas was admitted to the high vacuum side by small doses, but above this range so much nitrogen was necessary before the final pressure showed any appreciable increase that the modified method of introducing gas, described above, was used.

The charcoal bulb was surrounded by liquid oxygen for one hour before readings were commenced, otherwise it was found that the adsorption was erratic, due probably to inequalities of the temperature throughout the mass of charcoal.

At pressures lower than 10^{-3} mm. the time required for equilibrium to be attained was about 60 minutes, but at the highest pressures this time decreased considerably, and was 30 minutes at 8×10^{-2} mm. This time-effect may be due to diffusion within the apparatus.

* Phil. Mag. xlii. p. 246 (1921).

The air-temperature was noted at each pressure reading, and this value was used in calculating the quantity of gas adsorbed at N.T.P.

The results obtained with nitrogen are given in Table I.

TABLE I.

Adsorption of Nitrogen at −183° C.

p. Equilibrium pressure.	α. Quantity of gas adsorbed at N.T.P.	p. Equilibrium pressure.	α. Quantity of gas adsorbed at N.T.P.
$3{\cdot}0\times10^{-5}$ mm.	0·223 c.c.	$9{\cdot}72\times10^{-3}$ mm.	49·21 c.c.
6·4	0·336	13·11	54·48
$1{\cdot}16\times10^{-4}$	1·095	18·60	60·73
2·67	2·539	22·58	65·78
4·69	4·318	31·09	70·82
8·15	8·832	46·06	75·13
$1{\cdot}32\times10^{-3}$	13·54	55·99	77·33
1·99	22·14	70·30	79·77
4·38	39·11	79·75	81·31
6·66	44·16		

The relation between p and α is shown by curve (a), fig. 2. At pressures below $2{\cdot}5\times10^{-3}$ mm. the relation is linear, and may be represented by

$$\alpha = kp. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The results below 7×10^{-3} mm. are represented on a larger scale by curve (a), fig. 3.

The adsorption equation usually quoted,

$$\alpha = k\mathrm{P}^{\frac{1}{n}}, \quad \text{where P is in cm. of mercury,}$$

may be written in the form

$$\log\alpha = \log k + \frac{1}{n}\log \mathrm{P}, \quad . \quad . \quad . \quad . \quad (4)$$

and curve (a), fig. 4, shows the result of plotting $\log_{10}\alpha$ and $\log_{10}\mathrm{P}$. An examination of this curve shows that it consists of two parts, both of which are approximately straight lines. The values of $\frac{1}{n}$ for these portions have been determined; below 2×10^{-3} mm. it is 1·22, but above this point it changes to 0·20. This decrease of $\frac{1}{n}$ with increase in equilibrium pressure is in agreement with the conclusion of Claude * and Titoff †, and it was found that the adsorption isotherm given

* *Comp. Rend.* xlviii. p. 861 (1914).

† *Zeits. Phys. Chem.* lxxiv. p. 641 (1910).

by the author's results is similar in form to that deduced from Claude's results, but the quantities adsorbed in the present experiments are greater.

Considering the relation between α and P given in equation (1) and plotting $\log_{10} \frac{\alpha}{P}$ against α as shown by curve (a), fig. 5, there is a linear relation between these latter quantities above 2×10^{-3} mm. pressure ; below this pressure the relation is represented by a straight line parallel to the α axis, and this is to be expected if within the pressure range the relation between α and P is a linear one. The value of A_0 given by the horizontal portion is 5·0012.

b. *Hydrogen.*

Hydrogen was prepared by the electrolytic decomposition, between platinum electrodes, of freshly-boiled distilled water, acidified with pure concentrated sulphuric acid. The gas was passed over phosphorus pentoxide and stored.

The charcoal which had been used in the adsorption of nitrogen was outgassed by heating to 450° C. for 12 hours, the pumping arrangements maintaining the pressure below 10^{-5} mm. during the outgassing. Hydrogen was then admitted and, as in the case of nitrogen, a definite time was required for equilibrium to be attained, this time-interval decreasing as the pressure increased.

The results obtained for hydrogen are shown in Table II.

Table II.

Adsorption of Hydrogen at —183° C.

p. Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.	*p.* Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.
$7{\cdot}00 \times 10^{-4}$ mm.	0·0046 c.c.	$28{\cdot}59 \times 10^{-3}$ mm.	0·325 c.c.
9·44	0·0073	35·33	0·394
$1{\cdot}51 \times 10^{-3}$	0·0122	40·47	0·461
2·57	0·0231	46·09	0·515
3·40	0·0304	49·01	0·554
4·25	0·0403	54·06	0·604
5·83	0·0563	57·92	0·656
8·07	0·0781	62·70	0·708
12·21	0·126	68·67	0·760
15·72	0·170	73·00	0·806
19·36	0·212	77·83	0·857
22·81	0·255		

The adsorption isotherm is shown at (*b*), fig. 2. The isotherm appears to be a straight line and the relation

Fig. 2.

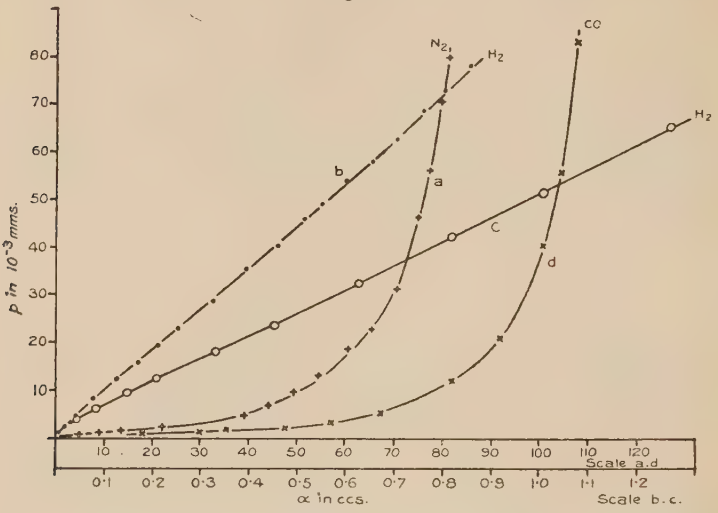
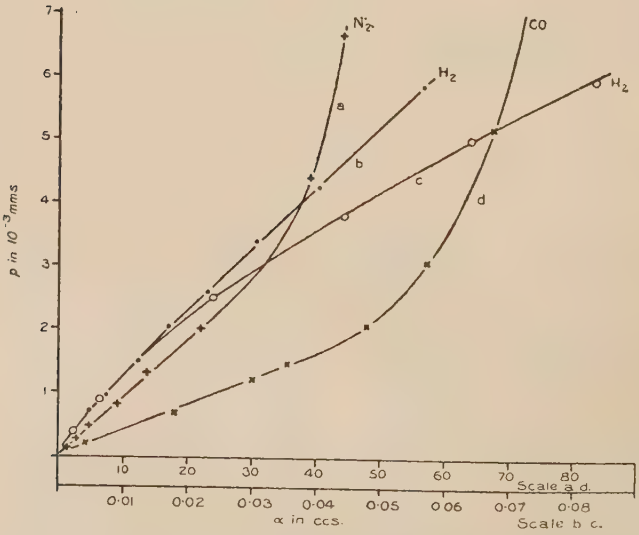


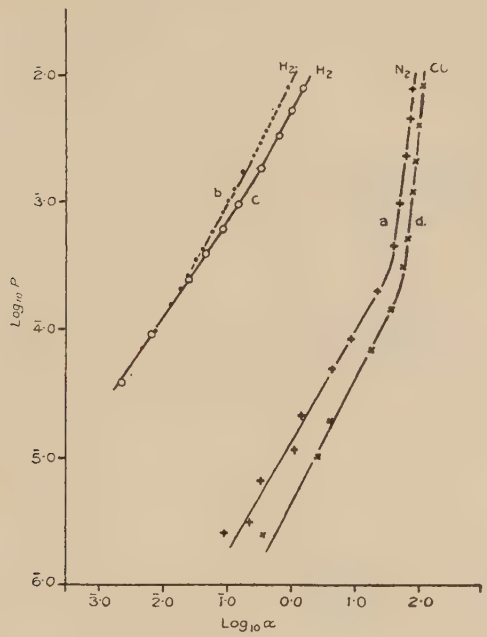
Fig. 3.



between α and p is approximately a linear one, but when the scale is increased, as shown at (*b*), fig. 3, the isotherm

becomes convex to the pressure axis at pressures below 5×10^{-3} mm.

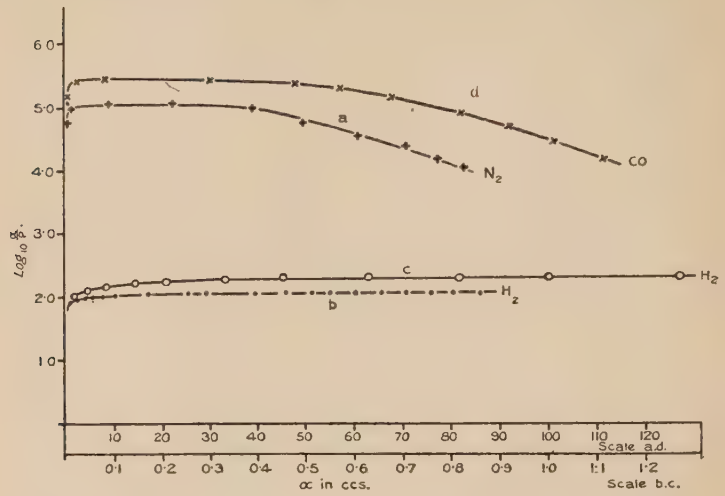
Fig. 4.



Since the relation between α and p is so nearly linear, it is to be expected that a graph showing $\log_{10} \alpha$ and $\log_{10} P$ would be a straight line as in (*b*), fig. 4. The value of $\frac{1}{n}$, deduced from this line, is 1·08, and is in close agreement with Titoff's statement that $\frac{1}{n}$ for hydrogen is unity at all pressures and temperatures. Similarly, $\log_{10} \frac{\alpha}{P}$ is constant and therefore is represented in (*b*), fig. 5, by a line parallel to the α axis. The value of A_0 from this graph is 2·0376.

The quantities of hydrogen adsorbed, as shown in Table II. are smaller than those obtained by Claude. It was suspected that the low results were due to gas previously adsorbed by the charcoal, and accordingly a sample of freshly reactivated charcoal which was initially thoroughly outgassed was used.

Fig. 5.



The values obtained with this second sample are given in Table III.

TABLE III.

Adsorption of Hydrogen at −183° C.

p. Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.	*p.* Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.
$3{\cdot}72\times10^{-4}$ mm.	0·0021 c.c.	$18{\cdot}04\times10^{-3}$ mm.	0·333 c.c.
8·91	0·0062	23·64	0·453
$2{\cdot}50\times10^{-3}$	0·0239	32·47	0·629
3·79	0·0446	42·12	0·821
5·95	0·0836	51·31	1·009
9·40	0·146	65·10	1·274
12·39	0·208	80·72	1·539

In these second experiments the volumes adsorbed are about 75 per cent. greater than those previously obtained.

The isotherms for hydrogen are shown at (*c*) in figs. 2 and 3, and the $\log_{10}$ relations at (*c*) in figs. 4 and 5. At pressures above 10^{-2} mm. there is a linear relation between p and α, but below this pressure the isotherm is convex to the pressure axis, even more so than in the first results for hydrogen. At pressures higher than 2×10^{-2} mm. the value of $\frac{1}{n}$, deduced from the curve (*c*), fig. 4, is 1·02. Below

this pressure the slope becomes less until curves (*b*) and (*c*) coincide; the value of $\frac{1}{n}$ for this portion is 1·03. The $\log_{10}\frac{\alpha}{P}$ curve possesses the same characteristics as the former hydrogen curve, becoming a straight line parallel to the α axis above 2×10^{-2} mm. and giving a value for $A_0=2{\cdot}2842$.

c. *Carbon monoxide.*

This gas was prepared by the action of warm concentrated sulphuric acid on formic acid. The evolved gases were first passed through a wash-bottle and scrubbing-chamber containing concentrated caustic potash solution which removed formic acid gas, and water-vapour was eliminated by passing the carbon monoxide over phosphorus pentoxide.

This gas was admitted to the charcoal in a manner similar to that adopted with nitrogen, and a "time-effect" was observed, due probably to diffusion, although the possibility of a time-effect within the charcoal itself is not to be excluded.

The results are given in Table IV.

TABLE IV.

Adsorption of Carbon Monoxide at −183° C.

p. Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.	*p.* Equilibrium pressure.	*a.* Quantity of gas adsorbed at N.T.P.
$2{\cdot}4\times10^{-5}$ mm.	0·339 c.c.	$3{\cdot}08\times10^{-3}$ mm.	57·17 c.c.
9·8	2·475	5·17	67·53
$1{\cdot}87\times10^{-4}$	4·007	11·80	81·88
6·77	17·96	20·75	91·82
$1{\cdot}20\times10^{-3}$	30·01	40·24	100·96
1·46	35·33	55·68	104·75
2·08	47·78	83·01	111·23

The adsorption isotherm (*d*), fig. 2, is similar to that for nitrogen, but the pressure below which the curve becomes a straight line is slightly less, being $1{\cdot}5\times10^{-3}$ mm.

The graph showing the connexion between $\log_{10}\alpha$ and $\log_{10}P$ (*b*), fig. 4, consists of two portions; the value of $\frac{1}{n}$ for pressures below $1{\cdot}5\times10^{-3}$ mm. is 1·41, but changes rapidly to 0·21 for higher pressures. The curve shown at (*d*), fig. 5, is similar to the corresponding nitrogen curve, the value of A_0 for the horizontal portion being 5·3830.

4. Discussion.

The adsorption isotherms are similar in shape to those obtained by other experiments working at higher temperatures and pressures. The nitrogen isotherm, at first straight, becomes concave to the pressure axis as the pressure increases. In this respect it differs from the isotherm at air-temperature, discussed in the previous paper, in which it was found to be convex to the pressure axis. The carbon-monoxide isotherm is similar to that for nitrogen. The hydrogen isotherm for charcoal which had been used in previous experiments is a straight line over practically the whole range of pressures used, but when drawn to a larger scale shows a slight convexity to the pressure axis at the lowest pressures. The isotherm for hydrogen using a fresh sample of reactivated charcoal has this convexity for a greater pressure range.

In all cases the quantities of gas adsorbed increase with their boiling-points.

At pressures below a critical pressure, which varies for the three gases, the adsorption isotherm is represented by

$$\alpha = k\mathrm{P}$$

or

$$\log_{10}\frac{\alpha}{\mathrm{P}} = \mathrm{A}_0.$$

This critical pressure is comparatively high for the gases of low boiling-point, but is considerably lower for those gases of higher boiling-point and which are more readily adsorbed by charcoal. Its value for nitrogen and carbon monoxide is $2{\cdot}0 \times 10^{-3}$ mm. and $1{\cdot}5 \times 10^{-3}$ mm. respectively. Hydrogen shows anomalous results, as even at high pressures the isotherm is a straight line, $\frac{1}{n}$ being equal to unity.

The value of the slope of the adsorption isotherm at the origin, derived mathematically from equation (1), is given by

$$\frac{d\mathrm{P}}{d\alpha} = \epsilon^{-2{\cdot}303\,\mathrm{A}_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The value of $\frac{d\mathrm{P}}{d\alpha}$ calculated from equation (4) is $9{\cdot}97 \times 10^{-6}$ for nitrogen, while the value obtained from the isotherm shown in fig. 3 is $9{\cdot}40 \times 10^{-6}$. The calculated and experimental values of this constant for hydrogen are $9{\cdot}17 \times 10^{-3}$ and $8{\cdot}88 \times 10^{-3}$ respectively, and for carbon monoxide $4{\cdot}14 \times 10^{-6}$ and $3{\cdot}92 \times 10^{-6}$ respectively. In the above

calculation the value of A_0 has been deduced from the horizontal part of the curves in fig. 5, as this corresponds to the linear relationship shown in the isotherms.

It was found that both at $-183°$ C. and at air-temperature a minimum equilibrium pressure is necessary before $\log_{10}\frac{\alpha}{P}$ becomes constant ; below this minimum pressure, the value of which varies with the different gases, the value of $\log_{10}\frac{\alpha}{P}$ increases with rise of pressure. This change cannot be explained, but it is present in all the gases so far examined at air-temperature as well as at $-183°$ C. It appears to be due to some physical property of adsorption at very low pressures. If $\log_{10}\frac{\alpha}{P}$ increases with α the adsorption isotherm must be convex to the pressure axis at these values, but the deviations from the linear relation at pressures below 10^{-4} mm. are not sufficient to state definitely that this is the case for nitrogen or carbon monoxide, although there is a definite convexity in the hydrogen curves.

As stated by Lamb, Wilson, and Chaney *, adsorption represents a balanced condition between the free-gas space and the surface film. The higher the concentration of free gas the greater will be the quantity adsorbed. The amount of adsorption as shown in fig. 2 is not in all cases, however, strictly proportional to the pressure. The lower parts, where a considerable amount of gas is adsorbed with very small increase in pressure, very probably represents the amount of gas adsorbed in a layer one molecule deep covering the active surface of the carbon.

That part of the curve which is concave to the pressure axis very probably represents the amount of gas which is held by the less firm and more variable adsorption of molecules in the second and third layers, and the tenacity of this adsorption depends to a considerable extent upon the curvature of the capillaries within the carbon.

One c.c. of carbon monoxide at N.T.P. spread in a layer one molecule deep so that the molecules are in contact with one another in a square formation occupies a surface area of 2·76 sq. metres. The adsorption isotherm for carbon monoxide begins to show a decided change in curvature

* Journ. Ind. & Eng. Chem. ii. p. 420 (1919).

after about 70 c.c. of gas at N.T.P. per gram. of charcoal have been adsorbed. Therefore, if this quantity is of unit molecular depth on the active surface of the charcoal, the minimum area occupied by it is 193 sq. metres. This value appears reasonable in view of the fact that activated charcoal has an estimated surface area of 2500 sq. metres per gram.

The shape of the adsorption isotherms can therefore be explained on the hypothesis given above. In the case of nitrogen and carbon monoxide the linear relationship holds until a layer one molecule deep is completed over the active surface, and the departure from this linear relationship represents the filling of the capillaries with layers of gas two and three molecules deep. The quantity of hydrogen adsorbed at the highest pressures in these experiments was not enough to saturate the molecular layer, and hence the isotherm remains a straight line over the whole range of pressures used.

5. Summary.

1. Results have been obtained for the adsorption of nitrogen, hydrogen, and carbon monoxide at very low pressures and $-183°$ C.

2. The adsorption isotherms have the same characteristics as those at higher pressures, and are better represented by

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha$$

than by

$$c = kP^{\frac{1}{n}}.$$

3. The connexion between α and P departs from a linear relationship after the active surface of the charcoal has been covered with a layer of gas of unit molecular depth.

In conclusion the author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research, and for the keen interest he has taken and the helpful suggestions made throughout.

XCVI. *Estimates of Geological Time, with Special Reference to Thorium Minerals and Uranium Haloes.*

By Arthur Holmes, *A.R.C.S., D.Sc., F.G.S., The University, Durham**.

Contents.

Introduction.
Solvent Denudation.
The Accumulation of Lead in Thorium Minerals.
The Loss of Lead from Thorium Minerals.
Pleochroic Haloes.
Cycles of Basaltic Fusion and Consolidation.
Conclusions.

Introduction.

Prof. Joly's recent work, conveniently summed up in 'The Surface History of the Earth' (1925), raises the question of geological time in an acute form. Joly suggests that geological history is made up of four or five successive cycles of basaltic fusion and consolidation. Each of these may, he thinks, have involved from 40 to 60 million years, giving a total of from 160 to 300 million years. It is then claimed that these figures are supported by the method of finding the age of the oceans from denudational statistics. By making certain assumptions the sodium method gives, according to Sollas, 175 million years as a maximum †. It is also suggested that the accumulation of thorium-lead in thorium minerals is more likely to give a trustworthy age determination than that of uranium-lead in uranium minerals. Joly refers to a thorite from the Palæozoic pegmatites of the Langesundfjord which revealed an age of only 150 million years ‡, and he states that thorium-lead ratios would probably indicate about 250 million years for all geological time. Against the greater ages calculated from analyses of uranium minerals it is urged that in remote times uranium may have disintegrated more rapidly than it does to-day. Support for this view is sought in measurements of uranium haloes in mica from granites of different geological periods. The older haloes are found to have a greater radius than the younger, whereas in the case of thorium haloes no such anomaly has been detected.

* Communicated by the Author.
† Q. J. G. S. vol. lxv. p. ciii (1909).
‡ See Table I., Analysis 9, and p. 1059 for comment.

While it is clear that the above results do not agree very happily among themselves, they do, nevertheless, favour comparatively low estimates of geological time, and they are definitely opposed to the longer estimates that have become familiar since Boltwood first suggested that lead might be the end-product of uranium. Evidently the whole of the data deserves a careful scrutiny, and I propose in this paper to examine it afresh.

Solvent Denundation.

The determination of the age of the oceans by the well-known sodium method has been widely discussed, and many geologists have rejected it as worthless*. In 'The Age of the Earth' (1913), I discussed the matter fully, and showed that the rocks would have to lose more sodium than they had ever contained in order to supply the amounts alleged to have been carried to the oceans by the rivers. So far as I know, no attempt has yet been made to refute this destructive argument.

For all the drainage areas of the world the estimated figures are as follows.—

Material carried annually to the Oceans.	Millions of Tons.
As sediment	5,700
In solution	2,440
Total	8,140
Sodium in solution	156

The sodium thus represents 1·9 per cent. of the material brought into the oceans. Of this material rather less than 90 per cent. is derived by erosion from the lands. The balance comes from the atmosphere and natural waters. The sodium therefore amounts to 2·1 per cent. of the material removed from the lands, according to denudational statistics.

The parent rocks of the eroded material consist of igneous and other crystalline rocks over roughly one-quarter of the area, and of sedimentary rocks over three-quarters of the area. The average sodium percentages in these rocks,

* J. W. Gregory: 'Nature,' Oct. 27, 1921, p. 283. A Harker: Proc. Yorkshire Geol. Soc. xix. p. 9 (1914). T. C. Chamberlin: Proc. Am. Phil. Soc. lxi. pp. 255–271 (1922). J. Barrell: Bull. Geol. Soc. Am. xxviii. p. 838 (1917).

according to the latest figures given by Clarke and Washington *, are :—

Igneous, 2·85 per cent.
Sedimentary, 0·81 per cent. } Average for the whole area, 1·32 per cent. of sodium.

Even if metamorphic rocks contained as much sodium as igneous rocks, which they do not ; and if all the crystalline rocks were to be denuded as rapidly as sedimentary rocks, which they are not ; and if all rocks were to lose all their sodium, which they do not ; then the total amount of sodium lost could not exceed 1·32 per cent. Actually they cannot lose on an average more than about 1 per cent. Yet river analyses imply a loss that is at least twice as great.

There are two ways, not mutually exclusive, of explaining away the obvious contradiction. Either the sodium in river waters is largely cyclic (and the invariable presence of chlorine supports this view), or the analyses of river waters for sodium are misleading. Sodium in the minute quantities present in river waters would be very difficult to estimate exactly, even if the utmost care were taken. It cannot be determined directly, but only as a final remainder estimated by difference, and the tendency of the errors is to give results uniformly too high. Whatever may be the reason, the estimate of the sodium carried to the ocean is certainly wrong. The method of determining the age of the oceans in which this estimate is the determining factor is at present based on utterly unreliable data ; and whether or not the method be sound in principle, the results derived from it cannot be allowed to carry any weight in settling the question of geological time.

The Accumulation of Lead in Thorium Minerals.

It is now well known that an isotope of lead (atomic weight 206) is the end-product of the uranium-radium series of elements, and that another isotope of lead (atomic weight 208) is the end-product of the thorium series. In primary uranium minerals the ratio of lead to uranium is approximately constant for minerals of the same geological age ; while in minerals of different geological ages, the older the minerals the higher are the lead-ratios. On the assumption that uranium has always disintegrated at the same rate as we find it to do to-day, the age of a uranium

* U.S. G. S. Prof. Paper, No. 127, 1924.

mineral is given to a first approximation by $\frac{Pb}{U} \times 6{,}600$ million years. In thorium minerals, however, the ratio of lead to thorium follows no ascertainable rule. Theoretically the age of a thorium mineral is given by $\frac{Pb}{Th} \times 18{,}000$ million years, or, reducing to the same factor as is used for uranium minerals, $\frac{Pb}{0{\cdot}37\,Th} \times 6{,}600$ million years. Some thorium minerals give the same ages as uranium minerals of the same geological age, but generally they give lower results which are discordant among themselves. In most radioactive minerals both uranium and thorium are present, and the age should therefore be given more accurately by taking both into consideration and using the formula $\frac{Pb}{U + 0{\cdot}37Th} \times 6{,}600$ million years *.

The variability in the amount of lead accumulated in thorium minerals of the same age has been a serious stumbling-block in the development of the radioactive methods of measuring geological time. In 1914, Dr. R. W. Lawson and I concluded from the evidence then available that lead could not be the end-product of thorium †. We suggested thallium as an alternative. Professor Soddy later suggested that only 35 per cent. of the lead might be stable, and that the remainder might disintegrate into thallium ‡. Later work has disproved both these hypotheses, and it is now generally accepted that all the lead produced from thorium is stable.

In 1917 Lawson attempted to explain the discrepancies by assuming that thorium minerals are in many cases secondary products, and consequently younger than the primary minerals with which they are associated §. The assumption, however, involves a geological improbability, and implies the action of a variable process which is difficult to formulate.

A somewhat different explanation is presented in this paper, but before discussing it, let us turn to the evidence of the minerals themselves.

Table I.—The minerals listed here are from the pegmatites associated with the nepheline-syenites of the Langesundfjord, thought by Brögger to be of Devonian age.

* The contraction m.y. is used hereafter.

† Phil. Mag. Dec. 1914, p. 824; and May 1915, p. 673.

‡ 'Nature,' Feb. 15, 1917, p. 469; and May 24, 1917, p. 244.

§ *Wien. Ber.* cxxvi. p. 721 (1917).

TABLE I.—Thorium Minerals of Devonian age from the neighbourhood of Brevik, Langesundfjord, Norway.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U+0·37Th).
1.	Uranothorite.	10·104	14·20	0·428	1·4	0·028
2.	Uranothorite.	8·93	44·24	0·297	4·9	0·012
3.	Uranothorite.	8·70	44·04	0·335	5	0·013
4.	Thorite.	1·48	51·84	0·76	35	0·036
5.	Thorite.	1·42	51·04	0·745	36	0·036
6.	Orangite.	1·183	45·03	0·054	38	0 003
7.	Orangite.	1·244	49·44	0·057	40	0·003
8.	Orangite.	1·02	63 05	0·82	62	0·034
9.	Thorite.	0·45	30·10	0·35	67	0·031
10.	Thorite.	0·70	47·25	0·076	68	0·004
11.	Thorite.	0 72	49·43	0·081	70	0·004
12.	Thorite.	0·407	29·20	0·020	72	0·002

1, 6, 7, 10, 11, 12. Phil. Mag. Dec. 1914, p. 832.
2, 3, 4, 5, 8. Dana's 'Mineralogy,' 6th Ed., p. 488.
9. Fajans: *Zeit. f. Elektro-Chem.* xxiv. p. 189 (1918).

The lead-ratios vary widely, and show no relation to the relative abundance of thorium. This is shown by the last two columns. Now if, as Joly supposes, uranium disintegrated much more rapidly in the past than it does to-day, then, in any series of the same age, the minerals relatively rich in uranium should give higher lead-ratios than those poorer in uranium but richer in thorium. The actual results give no support to the assumption favoured by Joly. The wide variability of the relations suggests the action of some process that has affected certain minerals and certain specimens more than others. There is only one kind of geological process which would have the observed consequences, and that is the partial leaching out of lead from the minerals concerned by weathering or by ground-waters.

Lead separated from the thorite analysed by Fajans (No. 9) was found by Honigschmid to have an atomic weight of 207·90. This is the mineral from which Joly calculates the age of the Devonian pegmatites as 150 m.y., although according to the ratio here given, 0·031, the age would be 205 m.y. On the assumption of integral atomic weights for thorium-lead and uranium-lead, the atomic weight, 207·90, would imply that the lead separated from the mineral consisted of 5 per cent. uranium-lead and 95 per cent.

thorium-lead. The age can now be calculated from each of the two isotopes :—

No. 9.—

$$\left.\begin{aligned}\frac{\text{Uranium-lead}}{\text{U}} \times 6{,}600 = 0{\cdot}039 \times 6{,}600 = 257 \text{ m.y.}\\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 = 0{\cdot}011 \times 18{,}000 = 198 \text{ m.y.}\end{aligned}\right\}$$

These results might be held to suggest either that uranium disintegrated more rapidly in the past, or that by leaching the mineral has lost more thorium-lead than uranium-lead. Unreasonable as the second alternative may seem to be at first sight, there are grounds for adopting it as being the hypothesis that on the whole coördinates the data most successfully.

Evidently the lead-ratios of Table I. are too variable to hold out any promise of a good determination. They seem to be, indeed, in the same position as the helium-ratios determined by Lord Rayleigh, which necessarily give only minimum results. The ratio 0·039 calculated from the uranium-lead of thorite No. 9 is likely to give the closest approach to the true age, though, if leaching has taken place, even this may be a minimum. It is noteworthy that other minerals from the same pegmatites but richer in uranium give ratios that average about 0·04 *.

Table II.—Most of the specimens of thorites and thorianites from Ceylon have been collected from gravels in which they are naturally concentrated. The minerals have, however, also been found *in situ* in certain pegmatites. These intrusions are younger than a group of zircon-bearing granites (Middle Pre-Cambrian age, lead ratio 0·16)†, which in turn are younger than the basal complex of crystalline limestones and gneisses. From a comparison of the Ceylon sequence with that of India, and that of East Africa, it seems most probable that the thorium pegmatites are of late Pre-Cambrian age, though the geological evidence does not preclude an early Palæozoic age. So far as is known, however, the minerals of Table II. are all of the same age, whatever that may be.

As in Table I., we find that the lead-ratios vary widely, from 0·017 to 0·075. The variation is independent of the proportion of thorium to uranium, though it is noteworthy that the thorites give lower ratios than the thorianites and are more variable among themselves.

* A. Holmes and R. W. Lawson : Phil. Mag. Dec. 1914, p. 832.

† A. Holmes and R. W. Lawson: Phil. Mag. Dec. 1914, p. 836, Analysis No. 9. A. Holmes : Q.J. G. S. lxxiv. p. 86 (1918).

TABLE II.—Thorium Minerals (and Pitchblende) from Ceylon. Age: Upper Pre-Cambrian or Palæozoic.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U×0·37 Th).
1.	Thorianite.	27·8	51·7	2·38	1·9	0·051
2.	„	26·8	57·0	3·5	2·1	0·073
3.	„	21·21	45·05	2·77	2·2	0·073
4.	„	24·8	54·9	2·16	2·2	0·048
5.	„	23·75	55·9	2·70	2·4	0·061
6.	„	23·0	55·0	2·78	2·4	0·064
7.	„	20·2	62·7	3·11	3·1	0·072
8.	„	13·1	67·3	1·87	5·1	0·049
9.	„	11·1	60·3	2·3	5·4	0·069
10.	„	11·8	68·9	2·34	5·8	0·063
11.	„	12·8	69·4	2·42	5·9	0·062
12.	„	11·4	69·5	2·36	6·1	0·063
13.	„	10·42	67·1	2·66	6·4	0·075
14.	„	9·5	63·7	2·10	6·7	0·063
15.	Thorite.	4·57	62·80	1·28	14	0·046
16.	„	3·50	59·2	0·78	17	0·030
17.	„	1·62	54·4	0·36	34	0·017
18.	„	1·88	65·38	1·71	35	0·065
19.	Pitchblende.	71·40	7·86	4·75	0·1	0·066

1, 4, 5, 6, 12. Analyst, Jones: Proc. Roy. Soc. A, lxxvii. p. 546 (1906).
2, 7, 10. „ Honigschmid: Privately communicated.
3, 18. Col. Reports, Misc. No. 74, Ceylon Cd. 5390 (1910).
8. Analyst, Ramsay: 'Nature,' lxix, p. 559 (1904).
9. „ Buchner: 'Nature,' lxxv, p. 165 (1906).
11, 13, 14. „ Blake: Proc. Roy. Soc. A, lxxvi, p. 253 (1905).
15, 16. Col. Reports, Misc. No. 87, Ceylon Cd. 7175 (1914).
17. Analysts, Soddy & Hyman: Trans. Chem. Soc. cv. p. 1404 (1914).
19. Col. Reports, Misc. No. 37, Ceylon, Cd. 3190, p. 38 (1906).

The three thorianites analysed by Honigschmid (Nos. 2, 7, and 10) are of special interest, as they represent the actual materials from which three samples of lead were extracted for atomic weight determination. The results obtained by Honigschmid * were:—

Lead from No. 2, 206·84 (58 % uranium-lead plus 42 % thorium-lead).
Lead from No. 7, 206·91 (54·5 % uranium-lead plus 45·5 % thorium-lead).
Lead from No. 10, 207·21 (39·5 % uranium-lead plus 60·5 % thorium-lead).

* Privately communicated.

The ages can now be calculated separately from each type of lead :—

No. 2.—

$$\left.\begin{array}{l}\dfrac{\text{Uranium-lead}}{\text{U}} \times\ 6{,}600 = 0{\cdot}076 \times\ 6{,}600 = 502\ \text{m.y.} \\ \dfrac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 = 0{\cdot}026 \times 18{,}000 = 468\ \text{m.y.}\end{array}\right\}$$

No. 7.—

$$\left.\begin{array}{l}\dfrac{\text{Uranium-lead}}{\text{U}} \times\ 6{,}600 = 0{\cdot}083 \times\ 6{,}600 = 548\ \text{m.y.} \\ \dfrac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 = 0{\cdot}023 \times 18{,}000 = 414\ \text{m.y.}\end{array}\right\}$$

No. 10.—

$$\left.\begin{array}{l}\dfrac{\text{Uranium-lead}}{\text{U}} \times\ 6{,}600 = 0{\cdot}078 \times\ 6{,}600 = 515\ \text{m.y.} \\ \dfrac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 = 0{\cdot}021 \times 18{,}000 = 378\ \text{m.y.}\end{array}\right\}$$

In each case the age calculated for the uranium-lead is somewhat higher than that calculated from the thorium-lead, but the results are definitely incompatible with Joly's claim that lead-uranium ratios may give results that are four times too high *. Joly bases this claim on a comparison of the ratio 0·066 given by pitchblende No. 19 with the ratio 0·017 given by thorite No. 17. But thorite No. 18 gives the ratio 0·065, and contains even less uranium relative to thorium than No. 17. There is clearly no reason whatsoever for picking out No. 17 as being correct while rejecting No. 18 as incorrect. Indeed, were it not for Honigschmid's exceptionally careful work, it would be difficult to resist the straightforward conclusion that the true ratio is of the order 0·066. It is possible that Joly based his age estimate on No. 17 alone, on account of the fact that Soddy determined the atomic weight of the lead separated from that particular thorite. Soddy obtained the value 207·74, and from the same material Honigschmid obtained 207·77, this being the mean value of three determinations. From the average of these results the uranium-lead is found to be 12 per cent. of the total lead, and the thorium-lead 88 per cent. of the

* 'The Surface History of the Earth,' 1925, p. 153.

total lead. The ages calculated separately are :—

No. 17.—

$$\left.\begin{array}{l}\dfrac{\text{Uranium-lead}}{\text{U}} \times\ 6{,}600 = 0{\cdot}026 \times\ 6{,}600 = 173\ \text{m.y.} \\ \dfrac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 = 0{\cdot}006 \times 18{,}000 = 101\ \text{m.y.}\end{array}\right\}$$

These results again disprove the contention that the uranium-lead ratio may be four times too high. What they do suggest is that lead has been leached out of the mineral (since the amount of lead now left is relatively so low), and that thorium-lead has now been removed to a greater extent than uranium-lead. The analysis of Honigschmid's results points to the same conclusion, as indeed do all the results of Table II.

On this hypothesis, which will be further discussed in a later section of this paper, the most nearly correct ratio for age-determination would be 0·083, obtained from the uranium-lead of thorianite No. 7. The thorium pegmatites of Ceylon would then be of the same age as the uraninite pegmatites of Katanga (lead-ratio 0·084) and the pegmatites of Brazil* (lead-ratio 0·084).

The Ceylon results still leave room for the possibility that uranium may have disintegrated more rapidly in former ages; but they also show that it has certainly not disintegrated four times as rapidly, and that the correction due to such possible variation, if any, is very small. This conclusion follows from the analysis of Nos. 2, 7, 10, and 17, and from the fact that many of the thorium minerals give ratios as high or higher than the pitchblende. The variability of the ratios must be almost wholly a consequence of irregular leaching.

Table III.—The pegmatites of the Arendal District which provide this suite of minerals are of Middle Pre-Cambrian age. Here, as in the other series, the data show that the lead-ratios do not depend on the relative richness in uranium. One of the thorites and one of the monazites give ratios of the same order as three of the uranium minerals. The thorium minerals, however, display a far greater variation among themselves than do the uranium minerals, and are clearly not reliable as indices of age.

* From a new analysis by E. P. Henderson, privately communicated by Prof. A. C. Lane

TABLE III.—Thorium and Uranium Minerals of Middle Pre-Cambrian Age from the neighbourhod of Arendal, Norway.

Ref.	Mineral.	U.	Th.	Pb.	Th/U.	Pb/(U+0·37 Th).
1.	Uraninite.	55·05	3·22	9·78	0·06	0·172
2.	Uraninite.	61·27	3·65	10·16	0·06	0·162
3.	Cleveite.	54·0	4·05	10·16	0·08	0·183
4.	Nivenite.	56·25	6·66	9·40	0·12	0·160
5.	Xenotime.	2·88	2·14	0·62	0·75	0·168
6.	Uranothorite.	8·80	45·50	1·55	5·2	0·160
7.	Orangite.	8·10	46·40	1·2[illegible]	5·7	0·049
8.	Monazite.	—	6·28	0·30	—	0·129
9.	Monazite.	—	8·45	0·53	—	0·166
10.	Monazite.	—	10·18	0·24	—	0·063

1, 2. Analyses by Hillebrand: U.S. G. S. Bull. 220, 1903, p. 114.
3, 4. Analyses by Hidden & Mackintosh: Hintze, *Mineralogie*, i. p. 1675.
5. Analysis by Blomstrand: *G. För. Förh.* ix. p. 185 (1887).
6 Analysis by Lindstrom: Hintze, *Mineralogie*, i. p. 1675.
7. Analysis by Hidden: Am. J. Sci. xli. p. 440 (1891).
8, 9, 10. Dana's 'Mineralogy,' 6th ed. p. 751.

It will be noticed that uraninite No. 1 gives a higher lead-ratio than No. 2, of which it is an altered variety. Cleveite, No. 3, is also an altered form of uraninite, and gives a still higher ratio. The analyses show that in the course of the alteration there is a loss of uranium, but, proportionately to the uranium, an actual gain in lead. This indicates that the lead in uraninites is present in a form that resists removal by leaching. Some of the thorium minerals, on the contrary, have lost lead, and therefore, if the percolating solutions responsible for the alterations have introduced lead into the altered uraninites, the added lead should be largely thorium-lead.

Fortunately it is possible to test this deduction by analysing the results for Cleveite, No. 3. Lead from this mineral was supplied by Mlle. Ellen Gleditsch to Messrs. Richard and Wadsworth, who determined its atomic weight as 206·084. The lead from cleveite therefore consists of 4·2 per cent. of thorium-lead and 95·8 per cent. of uranium-lead. Applying these proportions to the chemical analysis

of the mineral itself, we get :—

No. 3—

$$\left.\begin{aligned}\frac{\text{Uranium-lead}}{\text{U}} \times 6{,}600 &= 0{\cdot}18 \times 6{,}600 = 1{,}188 \text{ m.y.} \\ \frac{\text{Thorium-lead}}{\text{Th}} \times 18{,}000 &= 0{\cdot}106 \times 18{,}000 = 1{,}908 \text{ m.y.}\end{aligned}\right\}$$

Evidently the lead introduced must have been rich in thorium-lead, and this could only have come from thorium minerals undergoing leaching. In Table III. we have therefore definite evidence that the lead in thorium minerals is removed more readily than the lead in uranium minerals. Further, when lead is introduced into a uraninite undergoing alteration, it tends to be in part fixed there, presumably by the formation of a highly insoluble compound.

TABLE IV.—Thorium and Uranium Minerals of Pre-Cambrian Age from Llano Co., Texas.

Ref.	Mineral.	U.	Th.	Pb.	Pb/(U+0·37 Th.)
1.	Uraninite.	55·18	5·90	9·35	0·163
2.	Uraninite.	56·45	6·66	9·43	0·160
3.	Mackintoshite.	19·75	39·86	3·47	0·100
4.	Thorogummite.	19·70	31·40	2·01	0·064
5.	Yarrialite.	2·28	7·70	0·45	0·089

1. Hillebrand : Am. Journ. Sci. xlii. p. 391 (1891).
2. Mackintosh : Am. Journ. Sci. xxxviii. p. 481 (1889).
3, 4. Hillebrand : Am. Journ. Sci. xlvi. p. 101 (1893).
5. Hillebrand : Am. Journ. Sci. xiii. p. 149 (1902).

TABLE IV.—The minerals from Llano County, in Texas, are from pegmatites of Pre-Cambrian age, the associated granites being similar in general character to the Lorrian or Algoman granites *. With the exception of the uraninites, most of the minerals are far from fresh, and they are therefore of little value for age-determinations. Becker used them, or rather misused them, to cast doubt on the validity of the whole method of measuring geological time by lead-ratios. Barrell, however, in the paper cited *, has given a careful account of the evidence relating to the Llano minerals, and has pointed out that the uraninites give the same lead-ratios as Middle Pre-Cambrian minerals from Canada, Norway, Sweden, and Africa. To these localities

* J. Barrell, Bull. Geol. Soc. Am. xxviii. p. 862 (1917).

Ceylon may also be added. All give ratios of about 0·16 and together they provide a most valuable datum line for the correlation of Pre-Cambrian formations in widely separated lands.

The three thorium minerals (Nos. 3, 4, and 5) are inserted to show, as before, the tendency to loss of lead. Although no atomic-weight determinations have been made, direct mineralogical evidence is available showing the effects of alteration due to percolating waters. Thorogummite No. 4 is a yellowish brown residual mineral produced from mackintoshite No. 3 by oxidation and further hydration. Corresponding to this change, the lead-ratio is lower than that of mackintoshite, which in turn gives a lower ratio than the uraninites. Thus there is clear evidence that the thorium minerals have suffered a loss of lead just as was deduced in the case of those from other localities. The uraninites, on the contrary, are abnormal neither in oxidation nor hydration, showing that the ratios derived from them are not likely to have been vitiated by external interference.

The Loss of Lead from Thorium Minerals.

In every case for which data are available, thorium minerals, without exception, seem to have lost part of the lead that had accumulated in them, and, moreover, to have lost thorium-lead in greater proportion than uranium-lead.

Whenever atomic-weight determinations have made it possible to calculate the proportions of the two isotopes, the preferential abstraction of thorium-lead is clearly indicated :—

Table and No.	Mineral.	Age from Thorium-lead	Age from Uranium-lead.	Difference.
I, 9 ...	Thorite, Brevik.	198 m.y.	257 m.y.	30 per cent.
II, 2 ...	Thorianite, Ceylon.	468	502	7 „ „
II, 7 ...	„ „	414	548	32 „ „
II, 10 ...	„ „	378	515	36 „ „
II, 17 ...	Thorite, „	108	173	60 „ „

Had the Ceylon minerals not been interfered with by external agencies, then all the ages calculated in each way should have agreed, and should have been the same as those calculated from the ratio Pb/(U + 0·37 Th). It is impossible to explain the discrepancies either by assuming that the atomic weights of thorium-lead and uranium-lead depart slightly from the integral values (as quite probably they do), or by assuming slightly different values for the

half-periods of uranium and thorium. The possible presence of ordinary lead has also been considered, but that assumption equally fails to explain the anomalies, and is in any case unjustified by the mineralogical evidence. Galena does not occur in association with any of the minerals under discussion. Galena does occur with the pitchblende of certain mineral veins, but in pegmatites it is extremely rare.

Both uranium-lead and thorium-lead have chemical properties that are identical with those of ordinary (207·2) lead, and it may seem incredible that one should be removed from a mineral in greater relative amount than the other. There remains, therefore, the further possibility that both isotopes of lead have been leached out in the same proportion as that in which they were generated, but that uranium has disintegrated progressively more rapidly in the past. On this assumption the ages of the Ceylon minerals calculated from uranium-lead should be higher than those calculated from thorium-lead, and higher by the same percentage throughout the series. Reference to the above figures shows that the actual percentages vary from 7 to 60 per cent. The average percentage is 34 per cent., practically the same as that for the Brevik thorite (which is only half the age), instead of being more than twice as high, as it should be on the assumption made.

Clearly the hypothesis that thorium-lead is preferentially leached out is the only one that seems to provide an explanation.

Analyses of primary uranium minerals, on the other hand, rarely reveal any loss of lead ; and when they are altered by natural waters, the tendency is for lead, on balance, to be gained either absolutely or relatively to the uranium that is left. Table III. has already afforded excellent examples of this rule. Another case has been recorded recently by Ellsworth, who has carefully analysed uraninites from the Middle Pre-Cambrian pegmatites of Ontario. An externally altered specimen gave a ratio of 0·171 against an average ratio of 0·15 from five specimens not externally altered *. An altered uraninite of North Carolina gave a ratio of 0·053, whereas carefully selected material gave 0·049. An altered pitchblende from Gaya, India, gave nearly 0·2, while a fresh specimen gave 0·13.

This rule cannot, of course, be expected to hold when, as at Katanga, uranium minerals have been completely dissolved by ascending solutions and new secondary minerals deposited elsewhere, nor does it seem to apply to the

* H. V. Ellsworth ; Am. Journ. Sci. ix. p. 143 (1925).

pitchblende of Ceylon, of which, however, more analyses would be welcome. Uniformity of behaviour under the attack of altering processes is naturally not to be anticipated, and the fact that in so many cases altered uranium minerals do show an increase of lead is therefore the more significant.

It follows from the above considerations that in minerals the lead formed from uranium should exist in a relatively insoluble compound, and that the lead generated by thorium should exist in a more soluble compound. Now, when an atom of lead comes into existence in the crystal lattice of uraninite, it must be surrounded by atoms of uranium and oxygen; that is to say, it is in an acidic environment. Helium, being inert, need not be considered. It seems probable, therefore, that the general association of atoms should correspond to the assemblage required to form a molecule of lead uranate. At first the arrangement of atoms would be haphazard, but if water passed slowly through the crystal, the resulting localized mobility and kinetic exchange would promote at each point the formation of the most insoluble compound possible; that is to say, lead uranate. Moreover, if lead were introduced into the crystal lattice by water, one would expect that an interchange of atoms would then be possible, some of the lead being left and some of the uranium being removed. In this way the material left behind would become more insoluble than it was originally and the lead-uranium ratio would be increased.

In thorium minerals the lead could not form a thorate, as thorium and oxygen do not constitute an acidic environment, and corresponding with this no thorates are known to exist. In thorianite the lead should be largely present as an oxide; and in thorite partly as oxide, and partly perhaps as a silicate. In both minerals the most probable lead compounds are therefore of a comparatively soluble type.

In mixed minerals, such as thorianites rich in uranium, the tendency to loss of lead should be less than in thorites poor in uranium, as we find to be the case. This follows from the fact that the thorium-lead migrating out of a thorianite must pass through an assemblage of atoms many of which are uranium and oxygen. Part of the lead which would otherwise escape should thus be arrested and fixed as lead uranate. In thorites the corresponding capacity to retain lead is practically negligible.

The hypothesis of preferential leaching is thus in accordance with chemical probabilities, and for the first time the

long-puzzling discrepancies between thorium and uranium minerals appear to receive an adequate explanation.

Pleochroic Haloes.

In the course of his remarkable researches on pleochroic haloes, Joly * found that the uranium halo has a greater radius in micas from older granites than in those from younger rocks. The final results of his carefully confirmed measurements are these :—

Source of Mica.	Radius of Halo in mm.	Geological Age.
Mourne Mts., Ireland	0·0136	Tertiary.
Ballyellen, Ireland	0·0146	Devonian.
Rapakivi, Finland	0·0152	Late Pre-Cambrian.
Arendal, Norway	0·0155	Middle Pre-Cambrian.
Ytterby, Sweden	0·0160	

Since there is a definite relation between the rate of disintegration of an atom and the range of the α-particles it emits, Joly considers it probable that uranium or some part of it decayed more rapidly in the past than it does now, and that the rate, and consequently the radius of the resulting haloes, has gradually decreased through geological time. Thorium haloes reveal no variation of radius with age, and this points to some unique complication in the uranium series that is not shared by the thorium series. Further, it proves in the only way yet possible that the rate of disintegration of thorium has not varied during geological time. An alternative explanation of the uranium anomaly would thus clear the way towards using uranium haloes as evidence that the rate of disintegration of uranium has also been uniform, or practically uniform.

Several alternative explanations of the halo variations are possible. Some of these (such, for example, as depend on temperature changes in the rocks, long-range α-particles from the emitting centre, and direct collisions between α-particles and other elements) would require similar variations in thorium haloes, and therefore need not be considered.

I am indebted to my friend Dr. R. W. Lawson for directing my attention to the probable bearing of the actinium series on the problem. Uranium differs from thorium in giving rise to two distinct series of daughter

* Proc. Roy. Soc. A, cii. p. 682 (1923).

elements, one of them proceeding by way of radium (97 per cent.) and the other by way of actinium (3 per cent.). That the relation of actinium to uranium is a genetic one is established by the constancy of the ratio Ac/U in minerals.

A. S. Russell has given reasons *, based on empirical relations, for concluding that actinium arises from an isotope of uranium having an atomic weight of 239. He calculates the half-period of this hypothetical actino-uranium as about 8×10^9 years. If this be approximately correct, then in the past the relative abundance of actino-uranium must have been progressively higher. However, no one claims that the oldest haloes investigated by Joly are older than about 10^9 years, and consequently, within that period, the percentage of actino-uranium cannot reasonably be placed higher than 4 or 5 per cent. of the total uranium.

Such an isotope of uranium, or one of its daughter elements, would probably emit α-particles having the range required to explain the older haloes. As the percentage of actino-uranium would be small, the haloes due to it, or to its family, could not be visibly developed until after a geologically long period of time. In young haloes the effects of the actinium series would not be detectable at all. The actino-uranium halo, for example, would take at least twenty times as long to develop as the uranium halo. Moreover, once the subsidiary halo had reached the radius corresponding to the peak of the ionization curve, it would still tend to grow slowly outwards by the small amount corresponding to the last and less effective part of the range. The apparent radii of "uranium" haloes would therefore increase from younger to older examples, the later stages of growth taking place more slowly than the earlier. This deduction matches the actual data, as reference to the table on p. 1069 shows, for the time-interval between the Arendal and Rapakivi granites is roughly twice as long as that between the younger Irish granites.

If the above explanation be correct in principle, then the higher lead-uranium ratios would certainly be slightly too high, but not by more than 1 to 3 per cent. This conclusion is consistent with the atomic-weight determinations on lead from uranium minerals. The atomic weight of uranium-lead cannot be far from 206, and, according to Russell's interpretation of the actinium series, that of actinium-lead should be 207. Assuming integral atomic weights, then the mixed lead in minerals should be 206·04 or

* Phil. Mag. xlvi. p. 642 (Oct. 1923).

206·05 according as 4 or 5 per cent. of actinium-lead is present. The lowest value yet found is 206·046 for lead from the uraninite of Morogoro, Tanganyika Territory*. Lead from the Katanga uraninite has an atomic weight of 206·048 (and the mineral is free from thorium), and that from Bröggerite, Moss, Norway, with which a trace of thorium-lead must be associated, has an atomic weight of 206·06. These results show that if actinium comes from an undetected isotope of uranium, then the lead derived from it must have accumulated at practically the same rate as that followed to-day. Otherwise the atomic weights would be higher than they are. Even if in Middle Pre-Cambrian times the hypothetical isotope had been twice as abundant as it could be now, and the results do not admit so much as possible, then the age correction to be made would be a reduction of only 3 per cent. This would have to be slightly reduced to take into consideration the fact that uranium itself was more abundant then than now.

On the other hand, Joly's deduction that the larger lead-uranium ratios may be four times too high involves the assumption that at least 75 per cent. of the lead in any Pre-Cambrian mineral had been derived from an isotope that has now almost disappeared. Judging from all experience, this hypothetical isotope would have an atomic weight different from that of uranium as we know it, and therefore the atomic weights of the resultant lead in minerals should be expected to differ far more from 206 than they actually do.

Apart from Russell's views, it is at present generally considered likely that actinium arises from uranium II. This element disintegrates dually, 97 per cent. changing into ionium, the parent of radium, and 3 per cent. changing to uranium Y, which is thought to change to proto-actinium, the parent of actinium. In this case the apparent variation in the radii of the uranium haloes might be due to the cumulative effect of the α-activity of proto-actinium. Actinium itself is a β-rayer and does not generate a halo. As before, the effect superimposed on the normal uranium halo would become progressively visible to the maximum radius only after a very long period, the equilibrium amount of the emitting element being derived from only 3 per cent. of the original uranium. It is noteworthy that in the main or radium branch, ionium gives a halo of nearly the same radius as that of the alleged uranium halo of Ytterby mica.

This explanation, like that based on Russell's actino-uranium, is almost equally consistent with atomic-weight

* O. Honigschmid and St. Horovitz: *Wien. Anz.* 15th Oct., 1914.

evidence, and it requires no correction to lead-ratios since no isotope of uranium is implied.

It must finally be pointed out that the ranges of α-particles from uranium are not yet exactly known. The recent work of Gudden is itself based on uranium haloes in fluorspar, and cannot therefore be used as providing independent evidence *. No direct measurements have yet been made, and until that difficult task has been achieved, only intelligent speculation is possible based on empirical relations and guided by atomic-weight evidence.

Summing up, it is clear that the isotopic constitution of what we call uranium is not yet adequately known. The variable radii of uranium haloes can be explained in more ways than one. While Joly's deduction from that variation seems to be out of harmony with the ascertained atomic weights, those advanced here by Lawson and myself are consistent with them. In no explanation is it yet possible to appeal to the actual ranges of the α-particles from uranium, because these have not been directly observed.

Pleochroic haloes should therefore not be used to throw doubt on the validity of the lead-ratios, or to suggest a wide departure from a uniform rate of disintegration in the case of uranium. It is worth noticing, however, that Joly's measurements may afford a basis for a new method for determining within broad limits the ages of granites containing micas with haloes. By plotting time against halo-radii a scale is given by reference to which the ages of other measured haloes could be roughly estimated. The method requires extraordinarily careful measurements, and is therefore not to be lightly undertaken.

Cycles of Basaltic Fusion and Consolidation.

In a recent paper in the 'Geological Magazine' (Dec. 1925) I attempted to show that the surface history of the earth points to the interweaving of at least two different cycles of fusion and consolidation, one in the basaltic layer, and the other (with a much longer period) in an underlying layer assumed to be composed of peridotite or its chemical equivalent. This extension of Joly's brilliant conception is also in agreement with the longer estimates of geological time. Nevertheless, I consider that far-reaching hypotheses of this kind should not be regarded as providing any sort of method for estimating geological time, but should themselves be tested, and modified where necessary, by reference to the ascertained data of geological time-measurements.

* *Zeit. Physik*, xlvi. p. 110 (1924).

Conclusions.

A careful study of the evidence on which certain measurements of geological time have been based is consistently in favour of the longer estimates.

1. The sodium method fails for lack of reliable data and lack of adequate knowledge of the geo-chemical cycle of sodium salts (and particularly of sodium chloride in ground-waters) in geological processes.

2. Thorium-rich minerals give lead-ratios that vary from those of uranium minerals of the same geological age down to very low values. There is no reason why the lowest ratio should be regarded as the most reliable index to age. All are suspect, and none of them has much more value than a helium-ratio, which admittedly gives a minimum result. If uranium disintegrated more rapidly in the past, then there should be a relation between the lead-ratios and the ratio of thorium to uranium. The actual variation is quite irregular. Some thorium minerals give the same ratios as uranium minerals, and therefore there is no evidence that the uranium ratios are appreciably too high.

3. It is suggested that the discrepancies in thorium minerals are due to the fact that lead present as oxide or silicate would be more easily removed by percolating waters and kinetic exchange than the lead in uranium minerals, which may be present actually or potentially as a highly insoluble uranate.

4. Pleochroic haloes due to uranium provide no evidence that uranium has disintegrated more rapidly in the past, as Joly has contended. Other explanations are shown to be more probable as tested by atomic-weight evidence. One conjecture involves the possibility that a hypothetical actino-uranium of shorter life than uranium was formerly slightly more abundant than now. The reduction in the time estimates that would be necessary if this explanation were proved correct would range only between 1 and 3 per cent., not up to 300 per cent. as has been suggested.

5. Atomic-weight determinations on lead from uranium minerals support the view that uranium has always disintegrated at substantially the same rate as at present. At the worst, if the rate has varied it cannot have decreased (by the wearing-out of an isotope) by more than about 3 per cent. since Middle Pre-Cambrian times.

6. Finally, as a general deduction, we may safely assert that the evidence presented shows that the age of a fresh primary mineral free from ordinary lead is given to the

right order by the formula $\frac{Pb}{U+0{\cdot}37\,Th} \times 6{,}600$ million years. The factor 0·37 may later be found to be 0·35 or 0·38. The factor 6,600 may be 6,200 or 7,000*. A reduction varying up to 3 per cent. is necessary in all cases to take into consideration the obvious fact that the amounts of thorium and uranium now in a mineral must be less than those present when the mineral crystallized. A further reduction of 1 to 3 per cent. may in the future be found necessary if the parent of actinium should be identified with an isotope of uranium for which the name actino-uranium has already been proposed. Taking the outside limits of all combinations of the possible variables, the length of time that has elapsed since the crystallization of the Middle Pre-Cambrian pegmatites of Norway, Sweden, Ontario, Texas, and Africa is found to be between 930 and 1,080 million years, with 1,020 million years as the most probable value on present data. Higher ratios for the Lower Pre-Cambrian are known, but cannot yet be regarded as so well established as those for the Middle Pre-Cambrian.

It is my privilege, in conclusion, to express my thanks to Dr. R. W. Lawson, Professor Irvine Masson, and Dr. J. A. Smythe for their active interest in the problems of this paper; for discussing with me various points on which I sought their advice; and for their salutary criticisms and helpful suggestions.

XCVII. *Variation of Logarithmic Decrement with Amplitude and Viscosity of Metals.*—III. *By* G. Subrahmaniam, *M.A., A.Inst.P.*†

THIS is the third of a series of investigations which the author has undertaken in connexion with the variation of logarithmic decrement with amplitude and viscosity of metals. On the present occasion the study is extended to nine more metals, namely: gold, silver, platinum, tungsten, nickel, lead, tin, platinoid and phosphor bronze. Wires of gold, silver, lead and tin are made locally from very pure specimens of these metals, taking all possible precautions against their being "hollow drawn." Since gold, lead and tin in such pure forms are very soft and are easily deformed,

* Ellsworth gives this factor as 7,900 in an important paper on the Ontario uraninites and the subject generally (Am. Journ. Sci. p 133, Feb. 1925). The figure he adopts is quoted from an early paper by Lawson, and is based on old data which were faulty in regard to the half-period of radium.

† Communicated by Prof. A. L. Narayan.

these wires are kept straight and not wound on bobbins. The platinum wire is supplied by Smith & Co., of Madras, and is of guaranteed purity. The remaining wires—tungsten, nickel, platinoid and phosphor bronze are procured for us by Baird & Tatlock, of London, and are of good commercial quality, but not of absolute purity.

The method of experiment and the preliminary treatment to which each of the test wires is subject before it is finally taken to the vacuum chamber, are set forth in detail in my first communication *. I have, however, encountered certain difficulties with the soft metals—gold, lead, and tin—which have necessitated some modifications. In an attempt to keep each of them stretched by attaching a weight at the lower end these metals are found to "flow" perceptibly. Even a small weight long enough applied seemed sufficient to produce an appreciable effect, as, for instance, when the wires are kept loaded overnight. In these cases it is, therefore, found necessary to use moment of inertia bars of comparatively smaller masses, consisting essentially of two cylindrical brass pieces of equal mass and dimensions, fixed at the ends of a horizontal cross-piece, at equal distances from the axis of rotation. The bar used with the gold wire weighed about 124 grm., while that used with lead and tin wires only 38 grm. The moments of inertia of these two bars are determined experimentally by the usual method, and are found to be 1522 and 406·4 grm. cm.^{2} respectively.

With regard to lead and tin wires the zero, in addition, is found to be most erratic. The method of finding the logarithmic decrement under such conditions of unsteady zero affords an interesting illustration of the following theory of damped vibrations, suggested by Rowell †; but his assumption that A_0 is constant is by no means justifiable. We have, using Rowell's notation, the equation of motion in such cases:

$$m\ddot{x}+k\dot{x}+c^2x\pm F=0,$$

indicating that the system oscillates alternately about two origins distant $\frac{2F}{c^2}$ apart.

The solution of the above equation is evidently

$$x=\mp\frac{F}{c^2}-A_r'e^{-\frac{kt}{2m}}\cos(n_1t+\epsilon),$$

where

$$n_1=\sqrt{\frac{c^2}{m}-\frac{k^2}{4m^2}}.$$

* Phil. Mag. April 1925.

† Phil. Mag. July 1922, pp. 284–5; Nov. 1922, pp. 951–3.

In the above equation the sign of $\frac{F}{c^2}$ depends on $(-1)^r$ for the rth semi-oscillation. Hence

$$x=(-1)^r\frac{F}{c^2}-A_r'e^{-\frac{kt}{2m}}\cos(n_1t+\epsilon).$$

Put

$$A_r'=A_re^{-\frac{k}{2m}\cdot\frac{\alpha}{n_1}}\ \text{sec.}\,\alpha\,.\,d^r(-1)^r,$$

where

$$\cos\alpha=\frac{n_1}{\sqrt{\frac{k^2}{4m^2}+n_1^2}},\quad\text{and}\quad d=e^{-\frac{k}{2m}\cdot\frac{\pi}{n_1}},$$

the latter being obviously the decrement.

Also put $\frac{F}{c^2}=s$.

$$\frac{dx}{dt}=A_r'e^{-\frac{kt}{2m}}\left\{n_1\sin(n_1t+\epsilon)+\frac{k}{2m}\cos(n_1t+\epsilon)\right\}$$

$$=A_r'e^{-\frac{kt}{2m}}\left(\sqrt{\frac{k^2}{4m^2}+n_1^2}\right)\{\cos\alpha\sin(n_1t+\epsilon)$$

$$+\sin\alpha\cos(n_1t+\epsilon)\}$$

$$=A_r'e^{-\frac{kt}{2m}}\,.\sqrt{\frac{k^2}{4m^2}+n_1^2}\,.\sin(n_1t+\epsilon+\alpha).$$

We know $\dot{x}=0$ when $n_1t+\epsilon+\alpha=0$.

Let time be reckoned from $\frac{\alpha}{n_1}$ sec. after starting, so when $t=-\frac{\alpha}{n_1}$, we have $\dot{x}=0$.

$\therefore\quad -\alpha+\epsilon+\alpha=0$, thus making finally $\epsilon=0$.

So end of the first semi-oscillation is at time $\frac{\pi-\alpha}{n_1}$.

Again, because velocity is zero at beginning of second semi-oscillation, *i. e.* at time $\frac{\pi-\alpha}{n_1}$ $\quad\therefore\ \epsilon=0$,

similarly $\epsilon=0$ for the third semi-oscillation, and so on.

Generally $\dot{x}=0$ when $n_1t+\alpha=r\pi$, i. e. $t=\frac{r\pi-\alpha}{n_1}$.

$\therefore$ First semi-oscillation lasts from $-\frac{\alpha}{n_1}$ to $\frac{\pi-\alpha}{n_1}$.

Second . . . . . $\frac{\pi-\alpha}{n_1}$ to $\frac{2\pi-\alpha}{n_1}$.

. . . . . .

rth . . . . . $\frac{(r-1)\pi-\alpha}{n_1}$ to $\frac{r\pi-\alpha}{n_1}$.

During rth semi-oscillation

$$x=(-1)^r s-(-1)^r d^r \sec\alpha \,.\, \mathrm{A}_r e^{-\frac{k}{2m}\cdot\frac{\alpha}{n_1}} e^{-\frac{k.t}{2m}} \cos n_1 t.$$

So x_r, distance at the end of rth, is given by

$$x_r=(-1)^r s-(-1)^r d^r \sec.\,\alpha \mathrm{A}_r e^{-\frac{k}{2m}\cdot\frac{(r\pi-\alpha)}{n_1}} e^{-\frac{k}{2m}\cdot\frac{\alpha}{n_1}} \cos(r\pi-\alpha)$$
$$=(-1)^r s-\mathrm{A}_r.$$

Distance at beginning of rth or end of $(r-1)$th semi-oscillation is given by

$$(-1)^r s-(-1)^r d^r \sec.\,\alpha e^{-\frac{k}{2m}\cdot\frac{\alpha}{n_1}} e^{-\frac{k}{2m}\cdot\left\{\frac{(r-1)\pi-\alpha}{n_1}\right\}} \mathrm{A}_r \cos\{(r-1)\pi-\alpha\},$$
$$=(-1)^r s+d\mathrm{A}_r.$$

Similarly, distance at beginning of $(r+1)$th semi-oscillation is

$$(-1)^{r+1}s+d\mathrm{A}_{r+1},$$

and this is evidently equal to $(-1)^r s-\mathrm{A}_r$,

$$\therefore \quad d\mathrm{A}_{r+1}+\mathrm{A}_r=2(-1)^r s;$$

multiplying both sides by $(-1)^{r+1}d^r$, we have :

$$\mathrm{A}_{r+1}\,.\,(-d)^{r+1}-\mathrm{A}_r(-d)^r=-2sd^r$$
$$\mathrm{A}_r(-d)^r-\mathrm{A}_{r-1}(-d)^{r-1}=-2sd^{r-1}.$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\mathrm{A}_1(-d)'-\mathrm{A}_0=-2s.$$

$$\therefore \quad \mathrm{A}_r(-d)^r-\mathrm{A}_0=\frac{2s\,.\,(d^r-1)}{d-1},$$

$$\therefore \quad \mathrm{A}_r=\frac{1}{(-d)^r}\cdot\left(\mathrm{A}_0+\frac{2s}{d-1}\right)-\frac{2s}{d-1}(-1)^r.$$

Hence

$$x_r=(-1)^r s+\frac{2s(-1)^r}{d-1}-\left(A_0+\frac{2s}{d-1}\right)\frac{1}{(-d)^r},$$

and

$$x_{r+2}=(-1)^{r+2}s+\frac{2s(-1)^{r+2}}{d-1}-\left(A_0+\frac{2s}{d-1}\right)\frac{1}{(-d)^{r+2}}.$$

$$\therefore\quad x_{r+2}-x_r=\left(A_0+\frac{2s}{d-1}\right)\left\{\frac{1}{(-d)^r}-\frac{1}{(-d)^{r+2}}\right\}.$$

Similarly

$$x_{r+4}-x_{r+2}=\left(A_0+\frac{2s}{d-1}\right)\left\{\frac{1}{(-d)^{r+2}}-\frac{1}{(-d)^{r+4}}\right\}.$$

Finally

$$\frac{x_{r+2}-x_r}{x_{r+4}-x_{r+2}}=d^2.$$

Thus the decrement is found for lead and tin wires by noting three successive half-swings to the same side of zero.

Experimental Results.

In all these experiments the scale is, as usual, held at a constant distance of 74 cm., so that an amplitude of one cm. corresponds to an angular twist of 0·39 of a degree. The maximum twist to which each of the test-wires is subject is about 5°, except in the case of gold, lead and tin, where it is much smaller.

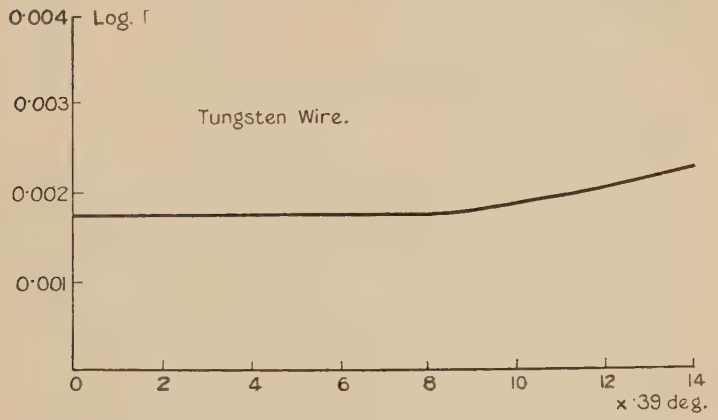
The experimental values are indicated in the accompanying graphs accurately. Tabular forms are, therefore, avoided from considerations of space. It will be seen from the graphs that the decrement-amplitude curves for tungsten, silver, platinoid and phosphor bronze wires run parallel to the x-axis until a limiting twist is reached, and thereafter increase, more or less linearly, with the amplitude, suggesting an equation of the form $\lambda_a=\lambda_0+f(a-m)$, where the constants "$a$" and "$m$" are, of course, different for different materials. These limiting twists are found to be 2·36, 2·58, 4·16, and 3·36 min. per unit length respectively. On the other hand, curves for platinum, nickel, and gold rise proportionately with the amplitude, and are therefore represented by $\lambda_a=\lambda_0+f(a)$. With regard to lead and tin wires no such detailed investigation is found practicable.

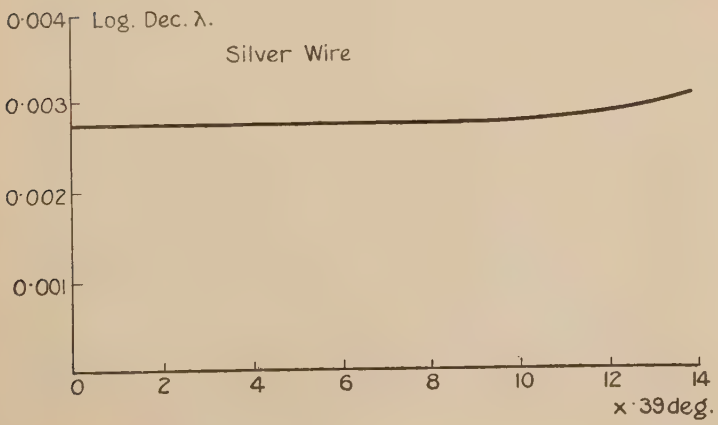
For purposes of calculation the log. dec. is extrapolated for zero amplitude, and the value substituted in the equation

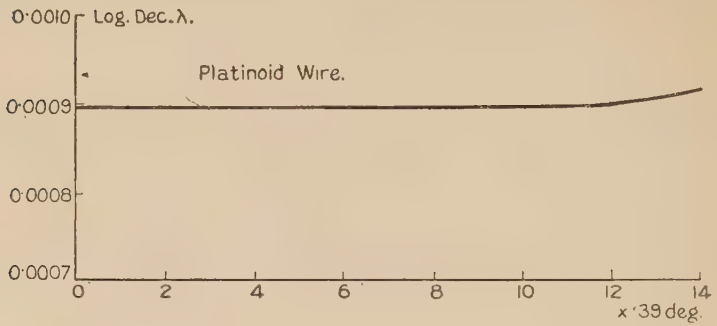
$$\eta=\frac{8Il\lambda_0}{\pi\,.\,T\,.\,R^4}.$$

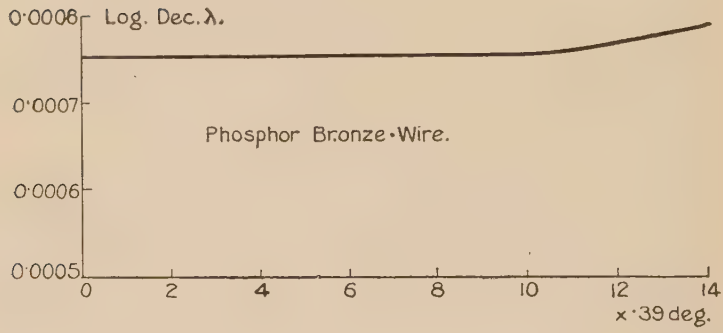
TABLE I.

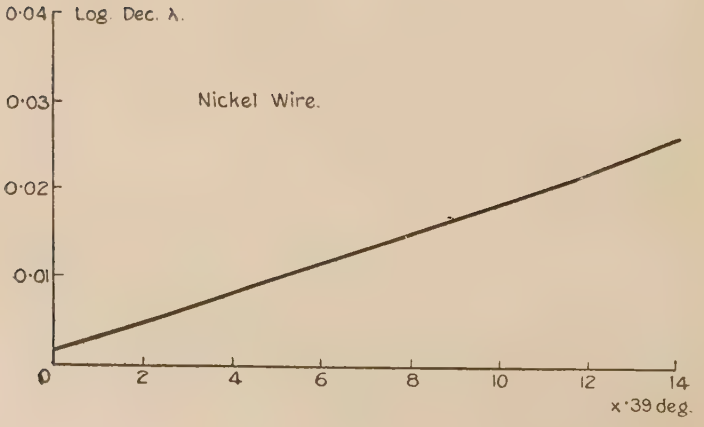
Metal.	I grm. cm².	l cm.	R cm.	T sec.	λ_0.	η poises.
Tungsten ...	3563	71·4	·02525	3·212	·001742	$8·638 \times 10^8$
Silver	,,	63·6	·02740	5·950	·002743	4·719 ,,
Platinoid ...	,,	65·8	·03025	3·367	·0008978	1·901 ,,
Phosphor bronze.	,,	71·0	·02525	5·997	·0007519	1·986 ,,
Nickel	,,	69·8	·02550	4·385	·001846	6·306 ,,
Platinum ...	3840·9	40·7	·01475	11·730	·0002381	1·707 ,,
Gold	1522	50·5	·02188	5·559	·007673	11·79 ,,
Lead	406·4	72·75	·03132	3·210	·06720	16·39 ,,
Tin.....	,,	71·55	·02525	3·630	·07124	35·72 ,,

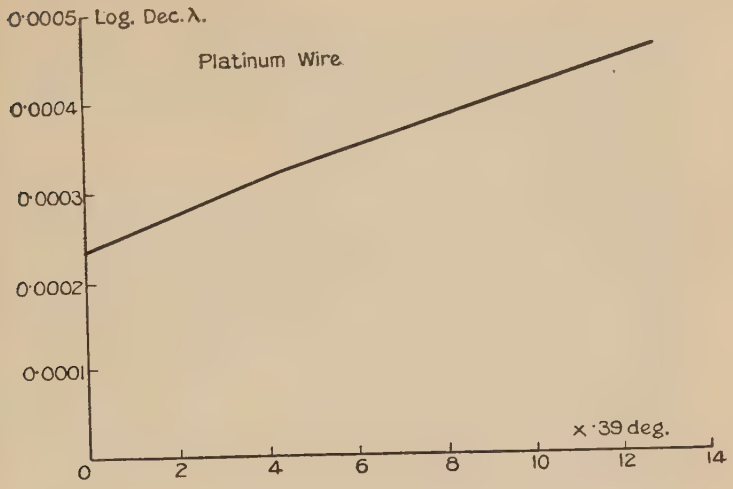


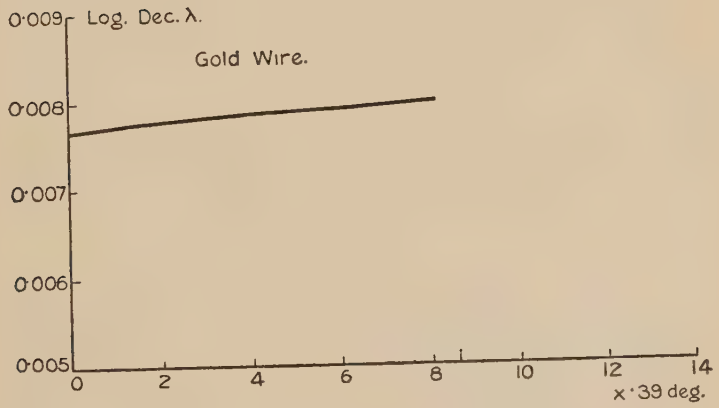



0·0010
Log. Dec. λ.
Platinoid Wire.
0·0009
0·0008
0·0007
0
2
4
6
8
10
12
14
x ·39 deg.


0·0008
Log. Dec. λ.
0·0007
Phosphor Bronze Wire.
0·0006
0·0005
0
2
4
6
8
10
12
14
x ·39 deg.


0·04
Log. Dec. λ.
0·03
Nickel Wire.
0·02
0·01
0
2
4
6
8
10
12
14
x ·39 deg.





The author, in conclusion, wishes to thank Prof. A. L. Narayan, M.A., D.Sc., F.Inst.P., for his stimulating interest in these investigations, and Prof. S. Purushotham, M.A., for valuable suggestions.

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XCVIII. *The Time of Excitation of Hydrogen Atoms.*

By J. S. McPetrie, *B.Sc., Aberdeen University**.

Summary.

Previous workers on the light-emission from a beam of positive rays have assumed that the time during which an electron remains in an excited orbit is negligible, and their aim has been the determination of the time of emission. The present paper has for its object the determination of this time of excitation, and it is shown to be comparable with the time of emission.

One method used gives the value of about 10^{-8} sec. for the time of excitation of the H_β line of the Balmer Series of Hydrogen.

A slightly different method is described for the determination of the values of both the times of emission and excitation. They are found to be approximately 2×10^{-8} sec. and $7{\cdot}5\times10^{-9}$ sec. respectively.

The slightly different results obtained for the time of excitation by the two methods are discussed, and reasons given for the small discrepancy.

On Bohr's Theory of Spectra an atom radiates energy when one of its extra-nuclear electrons returns from an unstable orbit to one of less energy, the frequency of the line emitted being given by the familiar equation

$$h\nu = E_1 - E_0,$$

where E_0 and E_1 is the energy-content of the atom when the electron responsible for the radiation is in the stable and unstable orbit respectively.

Wien in a number of papers (*Ann. d. Phys*, 1919–1925) describes extensive research on the light given out by the moving atoms in a beam of positive rays. Using a spectrograph of large dispersion, he has measured the intensity of light-emission at various distances behind the cathode at different pressures and velocities. In his latest paper † he measures the variation of intensity at a point a short distance from the cathode at low velocities and high pressures. On the assumption of a definite time of excitation (Verweilzeit) he shows mathematically that it cannot be distinguished by this method from the actual

* Communicated by Prof. G. P. Thomson, M.A.

† *Ann. d. Phys.* lxxvi. (Jan. 1925).

time of emission (Abklinungkeit) due to the symmetry of the equation. The expression for the intensity also seems to indicate that, as the pressure in the positive-ray tube is increased, the intensity at any fixed point in the positive beam should first increase and then diminish, the rate of decrease of the intensity and the pressure required for maximum intensity being governed by the relative values of the time of emission and the time of excitation. His experiments indicate no such diminution of intensity, and he concludes that there is no time of excitation distinct from the actual time of emission.

Dempster * has also worked on the measurement of the intensity of the light-emission from a beam of positive rays. He fired fast-moving positive rays into an evacuated observation space. As the pressure in this chamber decreased, the length of the visible beam of rays diminished to an approximately constant value. On measuring the velocity of the rays by the Doppler Effect, he found that this distance of visibility corresponded to a time of about 5×10^{-8} sec. This time represents the sum of the times of emission and excitation.

It will be seen by the above that the time of excitation has never been measured by any method without the intervention of the time of emission. The present paper describes an experiment made to determine whether there was a time of excitation and, if so, to measure its approximate value without having to consider the time of emission.

Consider a point A in the positive-ray beam. Suppose by means of a magnetic field we get rid of the atoms charged at A before reaching B not much further along the tube than A. The intensity of the light emission at B will be reduced due to the removal of the atoms which were charged at A, and which would have been emitting at B had it not been for their deflexion by the magnetic field. The magnetic field affects only the moving charged atoms at A. In the positive-ray beam, however, we have stationary and moving charged atoms and molecules. Stationary emitting atoms and molecules serve only to complicate matters enormously so their effect has to be nullified. This was done in the following experiments by studying the moved part of the H_β line of the Balmer Series of Hydrogen. This line Wien has shown is emitted by uncharged H atoms, and being also the most intense line in the positive-ray spectrum of H_2, suits our purpose admirably. It must thus be understood

* Phys. Rev. Feb. 1920, and Astr. Journ. lvii. (May 1923).

that whenever intensity is mentioned below, it refers to that of the moved line only.

For the purpose of reducing experimental results it is convenient to consider two cases :—

(*a*) High velocity positive rays.
(*b*) Medium and slow velocity positive rays.

(*a*) If there is a time of excitation, a charged atom before it can emit has to capture an electron and pass through the excited state. The time for this to occur may be sufficient to cause an atom charged at A to pass beyond B, a short distance further on, before it can begin to emit, if the velocity of the atom be sufficiently large. In this case all atoms charged at A and gradually being neutralized between A and B would be beyond B before they get into the condition for emission. If we deflect these atoms charged at A, we make no difference to the intensity of the moved line at B, as none of the particles deflected would have been emitting at B even in the absence of the magnetic field. At smaller velocities, however, there would be a change in intensity at B, as some of the atoms charged at A would have time to regain an electron, pass through the excited state, and be in a condition for emission at B. This means that, as we increase the velocity of the rays, we come to a stage at which on switching on a magnetic field between A and B sufficiently intense to deflect all atoms charged at A into an earthed metal tube, we can detect no difference in the intensity of emission at B. This condition is satisfied if there is a time of excitation and the velocity of the rays is sufficient to cause all the atoms charged at A to pass beyond B in the excited condition. We have thus a method of determining absolutely the time of excitation (if any) of H_β without the necessity of taking into account the time of emission.

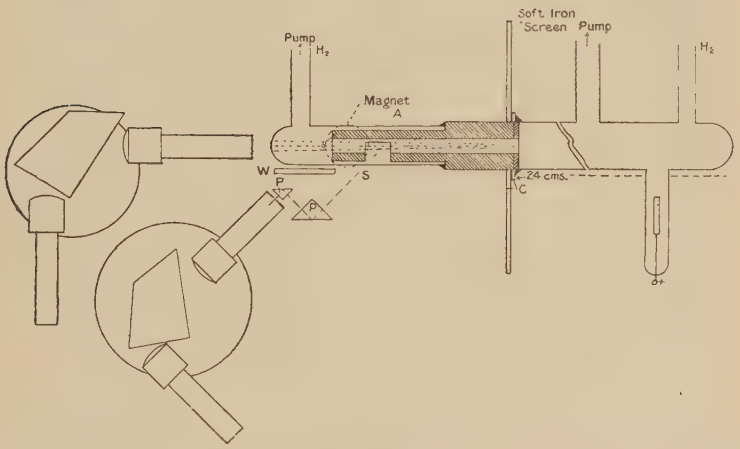
(*b*) In the general case of medium and slow velocity positive rays we can form an equation for the intensity at B with and without the magnetic field. This expression contains the times of emission and excitation as unknowns, the free paths in the charged condition being known from previous work by Ruchardt *. On measuring the decrease in intensity at B, brought about at various velocities and pressures on excitation of the magnetic field, we can determine, approximately, the magnitude of these times

* *Ann. d. Phys.* lxxi. p. 377 (1923).

separately, taking the value most nearly agreeing with that found in the case of the high-velocity rays as the time of excitation. Thus by using the result for the time of excitation found in (*a*), we can find the time of emission from the experiment made with medium velocity rays.

The apparatus consisted of a discharge-tube with an aluminium tube S 1·5 cm. long placed 7 cm. behind the cathode C in the path of the positive rays, the holes in S and C being parallel and each 0·5 cm. in diameter. The two chambers were thus at the same pressure, the large hole in the cathode being found necessary to obtain intensities sufficient for visual observation. A magnetic field could be excited transverse to the tube S by means

Fig. 1.



of a Du Bois magnet, MM, the strength of the field being sufficient to deflect all moving positive atoms in the beam into S, which was connected to C and to earth. A Hilger constant deviation spectrometer was placed to view the beam at B at an angle of about 45°. The prism P was arranged to reflect the light from A on to another reflecting prism covering the lower half of the slit of the spectrometer. Thus the image in the eyepiece of any line in the positive-ray spectrum of the gas in the discharge-tube consisted of two parts, the top half coming from A after two external reflexions and the bottom half from B viewed direct. In the mathematical expressions deduced below, it is the intensity of the moved line only that is considered; so a black screen was placed in the eyepiece

of the spectrometer to cut off the light from the long wave-length edge of the line under observation, the dispersion of the instrument not being great enough actually to separate the moving from the stationary line. An Ilford wedge-screen, W, could be passed in front of the top half of the slit of the spectrometer to reduce the intensity of the line seen in the eyepiece coming from B. This wedge was placed so as to make the two halves of the image in the eyepiece appear equally intense with no magnetic field across S when a reading of a scale attached to the wedge was taken. The magnet was then excited when the equality of intensity of the two halves of the image was destroyed, the top half being now brighter than the lower half. The wedge was therefore withdrawn until equality of intensity was again procured. A reading of the wedge-scale was again taken The wedges used in the two methods of determining the time of excitation described in (*a*) and (*b*) above had different indices, so the shifts in the two cases do not correspond numerically. It will be seen that by observing A and B at the same time, we get over the difficulty of any change in the discharge-tube conditions brought about by any stray magnetic field. Both parts of image, even when the discharge-tube is well screened, are slightly diminished in intensity on switching on the magnetic field ; but as it is the change in the relative intensity at A and B that is measured each time, the error due to this source is enormously decreased. A second Hilger spectrometer was placed to view the beam end-on in order to obtain a large reading for the Doppler effect. The pressure was also read. From these two measurements we can obtain the length of the free path of a positive atom, assuming it to be proportional to (Velocity)^3/Pressure *.

Table I. gives the measurements made with gradually increasing velocities.

The wedge-shift shown in the right-hand column of Table I. decreases with increasing velocity of the rays. This is shown in the accompanying graph (fig. 2), from which it will be seen that at a velocity of about $1{\cdot}5 \times 10^{-8}$ cm./sec. the shift of the wedge is too small to be detected. This means that the velocity of the atoms in the beam is sufficient to cause all atoms charged at A to travel a distance AB in the excited condition. The effect of the magnetic field, therefore, on the relative intensity of the beam at A and B is zero, as the atoms charged at A would not have

* Ruchardt, *Ann. d. Phys.* lxxiii. p. 228 (1924).

TABLE I.

Violet Edge. H_β.	Velocity.	Wedge-shift.
4853·1	$6{\cdot}7 \times 10^7$ c/s.	5·1 mms.
4850·6	$8{\cdot}27 \times 10^7$ „	5·0 „
4850·6	$8{\cdot}27 \times 10^7$ „	4·9 „
4851·7	$8{\cdot}2 \times 10^7$ „	4·9 „
4849·5	$8{\cdot}9 \times 10^7$ „	4·6 „
4845·35	$1{\cdot}13 \times 10^8$ „	3·3 „
4843·6	$1{\cdot}26 \times 10^8$ „	3·0 „
4840·7	$1{\cdot}43 \times 10^8$ „	1·1 „
4842·0	$1{\cdot}36 \times 10^8$ „	0·0 „

An actual set of readings is given below :—

Spark Gap ..... 0·303 cm.

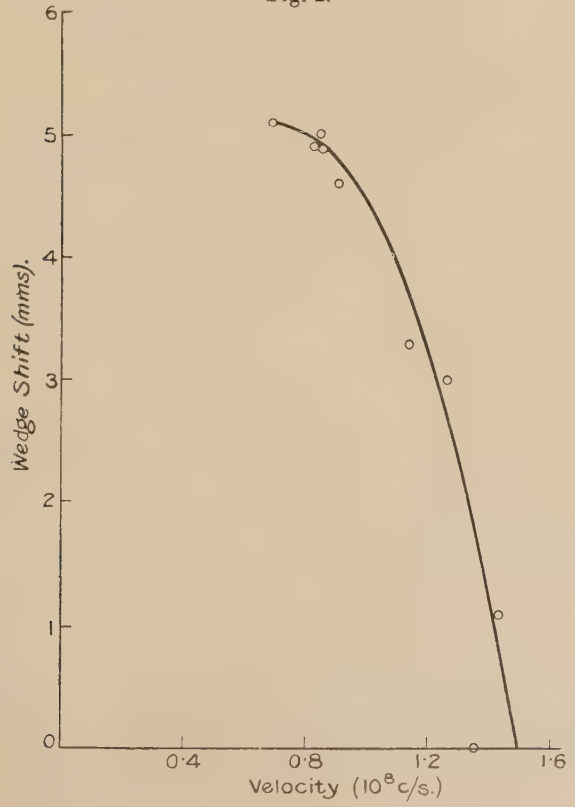
McLeod Gauge ..... 0·0258 mm. Hg.

Doppler Effect..... 4850 : 4851 : 4851 : 4850.

Wedge-scale readings ..... 2·6–2·1 : 2·4–1·9 : 2·3–1·9 : 2·35–1·85 : 2·4–2·6 : 2·38–1·9 : 2·38–1·88 : 2·4–188.

McLeod Gauge ..... 0·0248 mm. Hg.

Fig. 2.



begun to emit at B in the absence of the magnetic field. The distance AB is equal to the length of the earthed tube S (and of the magnetic field), which was 1·5 cm.

Let T be the time of excitation. Then we have

$$T = d/V,$$

where d is the length of the tube S and V the velocity necessary for zero shift.

$$\therefore\ T = 1{\cdot}5/1{\cdot}5 \times 10^{8}$$
$$= 10^{-8} \text{ sec.}$$

It should be noted that this method over-estimates slightly the time of excitation. This point, however, will be taken up in the discussion at the end.

We have now to consider the general case. Various expressions are obtained for the intensity of the light at the exit from the magnetic field corresponding to the different assumptions that are made as to the nature of the times of emission and excitation. In the following analysis it is assumed that all atoms remain in the excited condition for a definite time, and that the light emitted at x by a group of atoms N, all of which start to emit at $x=0$, can be represented by a function of the form KNe^{-bx}*.

Let N, N_1, and N_2 be the concentration of charged, emitting, and excited moving atoms at the entrance to the field. Let L be the mean distance moved by a charged atom before being neutralized, l the mean distance of emission, and λ the distance through which an atom moves in the excited condition.

Number of charged atoms per c.c. at entrance to field is N.

Number still charged at ξ

$$= N\left(1-\frac{\xi}{d}\right)e^{-\frac{\xi}{L}},$$

where d is the length of the magnetic field and $\left(1-\frac{\xi}{d}\right)$ is a factor introduced so that at distance ξ equal to d there are no charged atoms.

Number losing charge in element $\delta\xi$ at ξ

$$= \frac{N}{L}\left(1-\frac{\xi}{d}\right)e^{-\frac{\xi}{L}}\,\delta\xi.$$

* Although the equations obtained are different, the arithmetical value of I'_B/I_B found on substituting the various values for the time of emission does not vary much whether we assume that the atoms remain excited for a definite constant time or that the number still excited at x of N at $x=0$ is of the form KNe^{-cx}.

These remain excited until η, where $\eta-\xi=\lambda$, at which in an element equal to $\delta\xi$ they all begin to emit.

$\therefore$ Number beginning to emit in $\delta\xi$ at η $[\eta-\xi=\lambda]$

$$=\frac{N}{L}\left(1-\frac{\xi}{d}\right)e^{-\frac{\xi}{L}}\delta\xi,$$

$$=\frac{N}{L}\left(1-\frac{\eta-\lambda}{d}\right)e^{-\frac{\eta-\lambda}{L}}\delta\eta.$$

Intensity of light emitted at d due to these

$$=\frac{KN}{L}\left(1-\frac{\eta-\lambda}{d}\right)e^{-\frac{(\eta-\lambda)}{L}}e^{-\frac{d-\eta}{l}}.$$

$\therefore$ Total intensity of light-emission at d due to atoms charged at A

$$=K\int_{\lambda}^{d}\frac{N}{L}\left(1-\frac{\eta-\lambda}{d}\right)e^{-\left(\frac{\eta-\lambda}{L}\right)}e^{-\left(\frac{d-\eta}{l}\right)}d\eta,$$

$$=K\left\{\frac{Nl^2L}{d(L-l)^2}e^{\frac{\lambda-d}{L}}-\frac{Nl}{L-l}e^{\frac{\lambda-d}{l}}\right.$$
$$\left.+\frac{N\lambda l}{d(L-l)}e^{\frac{\lambda-d}{l}}-\frac{Nl^2L}{d(L-l)^2}e^{\frac{\lambda-d}{l}}\right\}.$$

The intensity of light at d due to atoms emitting at entrance to field

$$=KN_1e^{-\frac{d}{l}}.$$

Number of atoms per c.c. excited at entrance to field is N_2. Number of those beginning to emit in element $\delta\xi$ at ξ if $\xi<\lambda$,

$$=\frac{N_2}{\lambda}\delta\xi.$$

Intensity of light at d due to these

$$=\frac{KN_2}{\lambda}e^{-\frac{(d-\xi)}{l}}\delta\xi.$$

$\therefore$ Total intensity of light-emission at d due to atoms excited at entrance to field

$$=K\int_0^{\lambda}\frac{N_2}{\lambda}e^{-\frac{(d-\xi)}{l}}d\xi.$$

$$=\frac{KN_2l}{\lambda}e^{-\frac{d}{l}}\left(e^{\frac{\lambda}{l}}-1\right).$$

$\therefore$ Total intensity of emission at d due to all sources when magnetic field used

$$=K\left[\frac{Nl^2L}{d(L-l)^2}e^{\frac{\lambda-d}{L}}-\frac{Nl}{L-l}e^{\frac{\lambda-d}{l}}+\frac{N\lambda l}{d(L-l)}e^{\frac{\lambda-d}{L}}\right.$$
$$\left.-\frac{Nl^2L}{d(L-l)^2}e^{\frac{\lambda-d}{l}}+N_1e^{-\frac{d}{l}}+\frac{N_2l}{\lambda}e^{-\frac{d}{l}}\left(e^{\frac{\lambda}{l}}-1\right)\right] \quad . \quad . \quad \text{(i.)}$$

As observations were made at about 7 cm. behind the cathode, equilibrium must have been almost reached between the various constituents of the beam.

$$\therefore \frac{N}{L}=\frac{N_1}{l}=\frac{N^2}{\lambda}= \text{ some constant "}a\text{."}$$

$$\therefore N=aL : N_1=al \quad \text{and} \quad N_2=a\lambda.$$

Substituting these values for N, N_1, and N_2 in (i.), we obtain

$$\text{(i.)} \quad =K\left[\frac{aL^2l^2}{d(L-l)^2}e^{\frac{\lambda-d}{L}}-\frac{aLl}{L-l}e^{\frac{\lambda-d}{l}}+\frac{aL\lambda l}{d(L-l)}e^{\frac{\lambda-d}{L}}\right.$$
$$\left.-\frac{aL^2l^2}{d(L-l)^2}e^{\frac{\lambda-d}{l}}+ale^{\frac{\lambda-d}{l}}\right]=I'_B.$$

The intensity at A when no magnetic field used is proportional to N_1, the concentration of emitting particles at A.

$$\therefore \text{ Intensity at } A=KN_1=Kal=I_A.$$

Let T be the time of excitation and t the time of emission.

Then $$\lambda=TV \quad \text{and} \quad l=tV.$$

Substituting these values for λ and l in (i.), we get

$$I_B'=Kat V\left[\frac{Le^{\frac{TV-d}{L}}}{d(L-tV)^2}(LTV-TtV^2+LtV)\right.$$
$$\left.+\frac{e^{\frac{TV-d}{tV}}}{d(L-tV)^2}(dt^2V^2-L^2tV-tVLd)\right].$$

Also $$I_A=Kal=Kat V.$$

$$\therefore \frac{I_B'}{I_A}=\frac{Le^{\frac{TV-d}{L}}}{d(L-tV)^2}(LTV-TtV^2+LtV)$$
$$+\frac{e^{\frac{TV-d}{tV}}}{d(L-tV)}(dt^2V^2-L^2tV-tVLd). \quad . \quad . \quad \text{(ii.)}$$

In the steady state without the magnetic field the intensity of the moved line at A will be almost equal to that at B. Thus we may put $I_A = I_B$.

$$\therefore I_B'/I_B = I_B'/I_A = \text{eq. (ii.)}.$$

Eq. (ii.) therefore represents the ratio of the intensity at B with and without the use of the magnetic field. If by some means we could measure experimentally the ratio I_B'/I_B for various velocities of the positive rays, knowing L from Ruchardt's work, we could determine the values for T and t which on substitution in eq. (ii.) make it agree best with the measured values of I_B'/I_B in the different cases. It was for this reason that the Ilford wedge-screen was used as it measures directly the ratio I_B'/I_B. Let x be the shift of the wedge required to retain equality of intensity of the two halves of the slit in the spectroscope on switching on the magnetic field.

Then $$\log_{10} I_B'/I_B = -\mu x,$$

where μ is the index of the wedge.

There are two implicit assumptions made in the mathematical analysis above :—

(i.) That I_A does not change on excitation of the magnet.

(ii.) That the effect of the rays which lose an electron between A and B on the intensity of the moved line at B is small.

We shall consider these two points in detail.

(i.) The intensity at A does not necessarily remain the same when the magnet is excited. Suppose the intensity at A becomes cI_A where c is a fraction. The intensity at B will become cI_B'. Now the wedge measures the ratio of the intensities at A and B with the magnetic field divided by the ratio of the intensities without the field. That is, the wedge-shift gives us the value of

$$\frac{cI_B'/cI_A}{I_B/I_A} = \frac{I_B'}{I_B}.$$

The use of wedge therefore nullifies any error due to the change in the intensity at A on switching on the magnetic field.

(ii.) In the mathematics we assume that few of the moving ions produced between A and B emit at B. The graph obtained in the case of the higher velocities points to a time of excitation of about 10^{-8} sec. Ions produced within the region AB have to regain an electron and pass through the excited condition before they can emit. With the

slowest rays (7 or 8×10^7c/s) used this is sufficient to take them beyond B in the excited condition, provided they were not formed in the immediate neighbourhood of A. Those formed near A would have a very small effect, but the magnetic field was strong enough to deflect all ions formed near A into the earthed tube S between A and B.

Table II. gives a set of measurements with the value of I_B'/I_B in the column on the right calculated from the observed shift of the wedge.

TABLE II.

Velocity.	Wedge-shift.	I_B'/I_B.
$1{\cdot}3 \times 10^8$ c/s	·66 cm.	·64
$1{\cdot}2 \times 10^8$ c/s	·53 ,,	·70
$1{\cdot}02 \times 10^8$ c/s	·54 ,,	·69
$0{\cdot}95 \times 10^8$	·67 ,,	·64
$0{\cdot}92 \times 10^8$	·72 ,,	·62
$0{\cdot}83 \times 10^8$	·63 ,,	·66
$0{\cdot}80 \times 10^8$	·53 ,,	·70
$0{\cdot}79 \times 10^8$	·52 ,	·71

The magnitudes of the times of emission and excitation which make eq. (ii.) agree best with the measured values of I_B'/I_B for the various velocities are found to be 2×10^{-8} sec. and $0{\cdot}75 \times 10^{-8}$ sec. respectively. In Table III. are given the velocity, the observed value of I_B'/I_B and that calculated from eq. (ii.) on the assumption that t is 2×10^{-8} sec. and T $0{\cdot}75 \times 10^{-8}$ sec. It will be seen that the measured and calculated values of I_B'/I_B agree remarkably well, considering the rate at which eq. (ii.) varies with the values for the times of emission and excitation used in calculating it.

TABLE III.

Velocity.	I_B'/I_B (meas.).	I_B'/I_B (calcul.).
$1{\cdot}3 \times 10^8$	·64	·68
$1{\cdot}2 \times 10^8$	·70	·74
$1{\cdot}02 \times 10^8$	·69	·72
$0{\cdot}95 \times 10^8$	·64	·67
$0{\cdot}92 \times 10^8$	·62	·69
$0{\cdot}83 \times 10^8$	·66	·63
$0{\cdot}80 \times 10^8$	·70	·60
$0{\cdot}79 \times 10^8$	·71	·60

We thus find by the second method that the time of emission is about 2×10^{-8} sec., and the time of excitation $0{\cdot}75 \times 10^{-8}$ sec. The latter agrees as well as could be

expected with that found by the first method, viz. 10^{-8} sec. The difference is small, and can easily be accounted for, as the no wedge-shift method tends to make the result for the time of excitation slightly too big. This is due to the fact that, as the velocity of the positive rays increases, the intensity of the moved line of H_B rapidly diminishes, making observations difficult and, at the same time, the wedge-shift becomes smaller. The result of these two effects is that, before the wedge-shift should be zero, the intensity of H_B and the wedge-shift have both become so small that the latter is almost indetectable. Thus we declare that no shift of the wedge is required for less than the real minimum velocity necessary for no change in intensity to occur at B on switching on the magnetic field. The time of excitation is found by dividing the distance between A and B by the critical velocity which, being probably slightly too small, makes the time of excitation correspondingly too large.

No published paper has described a method for determining the time of excitation of any line of the Balmer Series of Hydrogen without the intervention of the time of emission. The entrance of these two times into any expression for the intensity of light-emission from a beam of positive rays makes discrimination between them difficult, if not impossible. By the no wedge-shift method, however, we can determine definitely the time during which an electron remains in an excited orbit without any regard being paid to the time it takes to liberate its quantum of radiation. Having found the time of excitation in this way, the time of emission may be determined explicitly by the second method. No ambiguity between the times of emission and excitation will then arise, as the latter must correspond with the value found for the time of excitation by the no wedge-shift method. Dempster obtains 5×10^{-8} sec. as the sum of the times of emission and excitation. The present paper gives a value of about 3×10^{-8} sec. There is, therefore, consistency between the two measurements ; but whereas up to the present the time of excitation has been assumed to be extremely small and almost a different way of looking at the time of emission, the above results indicate that it is distinct from the time of emission and comparable with it in magnitude. Stark * fired fast-moving positive rays into a space where the Electric Potential Gradient was very large. He found that the Stark effect at any point corresponded with the field very close to that point. This would indicate, in my opinion, a very short time of emission

* *Ann. d. Phys.* xliii. p. 968 (1914) ; xlviii. p. 194 (1915).

and a rather longer time of excitation. We must assume a time of excitation in this case to bring Stark's measurements into agreement with the rate of decay of emission in the beam as found by Wien. If there were no time of excitation, the rate of decay would be much larger than that observed. Another factor which points to a finite time during which an electron remains in an excited orbit is the definite frequency of the emitted spectrum line. This entails a sharply-determined quantized motion of the electron in the excited orbit which, I think, requires a finite time for the electron to assume it.

I should like to express my sincere thanks to Prof. G. P. Thomson, whose many suggestions and kindly criticisms have made possible the publication of this paper. Thanks are also due to the Robbie Trustees, Aberdeen University, for a grant during the progress of the work, and to Mr. S. A. McKay for valuable help in the taking of measurements.

National Physical Laboratory,
Teddington,
Jan. 24, 1926.

XCIX. *Ignition of Gases by Sudden Compression.* *By* H. T. Tizard, *F.R.S.*, *and* D. R. Pye *.

[Plate XVII.]

1. IT is well known that the ignition of gases by sudden compression can be qualitatively explained by the theory that at the temperature of compression the gases react at such a rate that heat is evolved by the reaction faster than it is lost by conduction to the walls of the vessel. In a previous paper † this theory was developed on a quantitative basis, and it was shown that with simple assumptions it could be shown to account completely for the delay that takes place between the attainment of the maximum compression temperature and the actual initiation of the explosion. From observations of the delay period at different temperatures above the minimum ignition temperature, it was found possible to deduce approximately the temperature coefficient of the reaction, and from this to calculate the change in ignition temperature when the rate of loss of

* Communicated by the Authors.
† Phil. Mag. July 1922.

heat was altered arbitrarily by stirring the gases violently during compression. The object of the experiments described in this paper was to examine the theory more closely and to clear up some doubtful points.

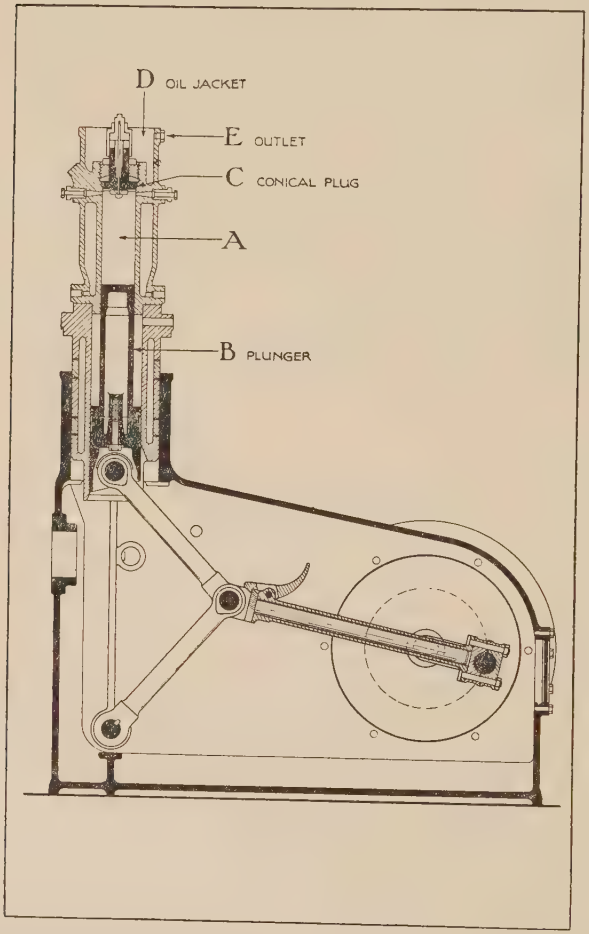
2. For this purpose a modified apparatus was designed and built, which has the advantage that it can be used for experiments with simple gases, such as hydrogen, which have fairly high ignition temperatures in the presence of air or oxygen. If the initial temperature of the gas before compression is low, high compression temperatures can only be reached by employing high degrees of compression. Thus Dixon and Crofts showed that a mixture of hydrogen and air initially at room temperature had to be compressed in the ratio of 15 : 1 before ignition occurred. The excessive compression pressures so produced cause considerable experimental difficulties when the compression cylinder is large. To avoid these difficulties, the initial temperature of the gas must be high. In our old apparatus it was impossible to heat the gases initially to a temperature much above 60°, since higher temperatures destroy the cup-leathers on the piston, which contain the oil seal necessary to keep the cylinder gastight. In our new apparatus this was overcome by arranging two cylinders in tandem. The upper cylinder contains a plain closely-fitting plunger, and it can be heated to 150–180° C. by an oil jacket. The lower cylinder is always kept at room temperature, and its piston is fitted with the double cup-leather and oil seal described in the earlier paper. On compression, the pressures in the lower and upper cylinders balance, so that there is no tendency for the gas in the upper working cylinder to escape. The general arrangement is shown in the diagram fig. 1. The indicator of the Collins type, used to record the changes of pressure of the gas, was described in detail by Pye*. The reproductions of records given in this paper are enlarged about eight times.

3. The working cylinder has a diameter of 3 inches, and the stroke of the piston is 8 inches. The machine can be arranged to compress in a ratio of either 6 : 1 or 9 : 1. But for the cylinder construction the apparatus is practically the same as the previous apparatus. Special attention may be drawn to the method of compression, which ensures that the piston cannot move outward and expand the gases after the maximum compression has been reached. This is an important feature of the apparatus, for, as the delay before ignition occurs is often as long as half a second, the volume

* 'Journal of Scientific Instruments,' March 1925.

of the compressed gases must be kept constant during this time. It is difficult, however, with an apparatus of this type to compress the gases very suddenly, owing to the

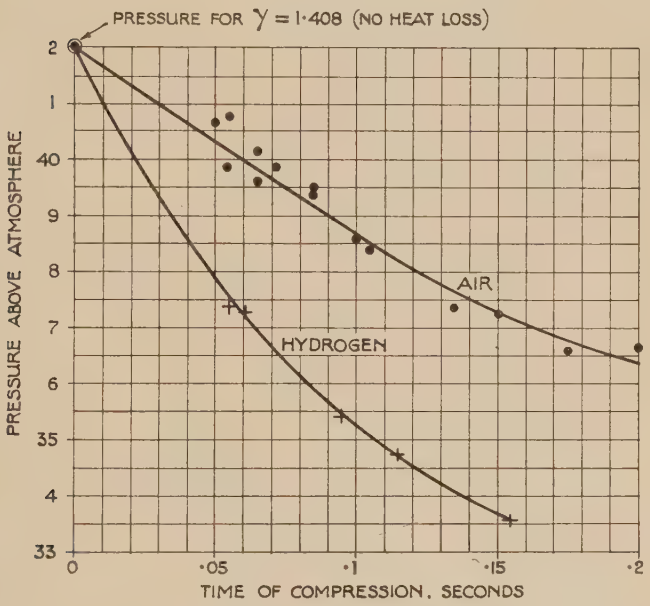
Fig. 1



inertia of the moving parts. We found that it was necessary for the time of compression to be greater than 0·05 second to avoid fracture of the moving parts; indeed, fracture occurred on one occasion when the time was as short as this, so that as a rule the time of compression was kept constant at 0·14 second.

4. Under these conditions the maximum pressure reached by compression is always considerably lower than that calculated on the assumption that compression is adiabatic. For instance, the pressures when air and hydrogen are compressed in the ratio of 6·09 : 1 was found to be 11·7 atmospheres for air and 10·7 atmospheres for hydrogen, when the time of compression was 0·1 second. The corresponding adiabatic compression pressure is calculated to be 12·5 atmospheres ($r = 1{\cdot}4$). The difference may be due to (*a*) gas leakage, (*b*) an increase in the average specific heat

Fig. 2.



of the gases due to the presence of water vapour or oil vapour, (*c*) loss of heat during compression. Special experiments showed that the possible effects of (*a*) and (*b*) were negligible. The rate of gas leakage was shown by these experiments to be less than 1 per cent. of the rate of fall of pressure due to cooling, while the compression of damp air when the surfaces of the piston and cylinders were freely lubricated with castor oil gave a value for the compression pressure only slightly less than that observed when dry air was compressed in a clean cylinder. That the pressure difference would be entirely accounted for,

within the limits of experimental error, by the loss of heat during compression was shown by carrying out a series of compressions of air and hydrogen at different rates of compression. The results of these experiments are shown in fig. 2, the pressures reached being expressed in arbitrary units—1 atmosphere being equal to 3·64 units. The lines through the observed points, when produced backwards, cut the pressure axis (which corresponds to instantaneous compression and no heat loss) at just about the "adiabatic" pressure.

It is of some interest to note here that in an internal combustion engine operating at 1200 r.p.m. the time of compression is 1/40th of a second. From the results shown in fig. 2, it appears that the loss of heat during the compression would not be greater than that corresponding to a 2 per cent. loss in compression temperature, even with a jacket temperature the same as that of the charge at the beginning of compression. For all practical purposes, therefore, it is safe to assume adiabatic compression in a high-speed internal combustion engine.

5. It is thus clear that the average temperature of a gas after compression will always be considerably lower than the adiabatic compression temperature. This raises the question whether the average temperature or the calculated adiabatic temperature should be taken as the ignition temperature when ignition occurs. In the work carried out by Dixon and others no pressure records were taken, and the calculated adiabatic temperature has therefore always been chosen. In our previous paper we gave our results in terms of the average temperature reached on compression, but we pointed out the uncertainty involved. This question has now been examined more closely.

The assumption that the gas after compression is uniformly at the same temperature except within a region quite close to the containing walls is clearly unjustifiable, though it may be sufficiently near the truth for all practical purposes. The more highly turbulent the gas, the more uniform will be the temperature. If it were uniform, we should expect the slow chemical reaction during the pre-ignition period to take place throughout the gas. If this were so, the pressure reached on compression would either remain constant or rise slightly during the delay period; and when ignition occurred the whole mass of gas would ignite at once. Dixon's photographs of ignition after compression throw light on this point. He showed that the start, as well as the spread, of ignition was very

indefinite, when compared with ignition started by a spark. On the other hand, it is quite clear from his photographs that the whole mass of gas does not ignite at the same moment. Our pressure records show that, though in some cases the compression pressure remains constant or rises slightly during the delay period, these cases only occur when the compression temperature is substantially higher than that corresponding to the least compression necessary to cause ignition. In fig. 3 (Pl. XVII.) a record is reproduced showing practically constant pressure during the delay period. In this case the time of compression was slow. In the majority of cases at or near the minimum ignition temperature there is a fall of pressure during the delay period, such as is shown on the record fig. 4 (Pl. XVII.) between 0·14 (end of compression) and 0·39 seconds, and this fall can occur at a rate which is practically the same as the rate of fall of pressure when no ignition occurs.

For instance, of twelve experiments on mixtures of octane and air under different conditions of temperature and mixture strength, eight ignited and four did not. The observed falls in pressure during the first and second, 1/10th of a second after the completion of compression are shown in the following table :—

TABLE I.

Pressure drop from $P_{max.}$ in lb. per sq. in.

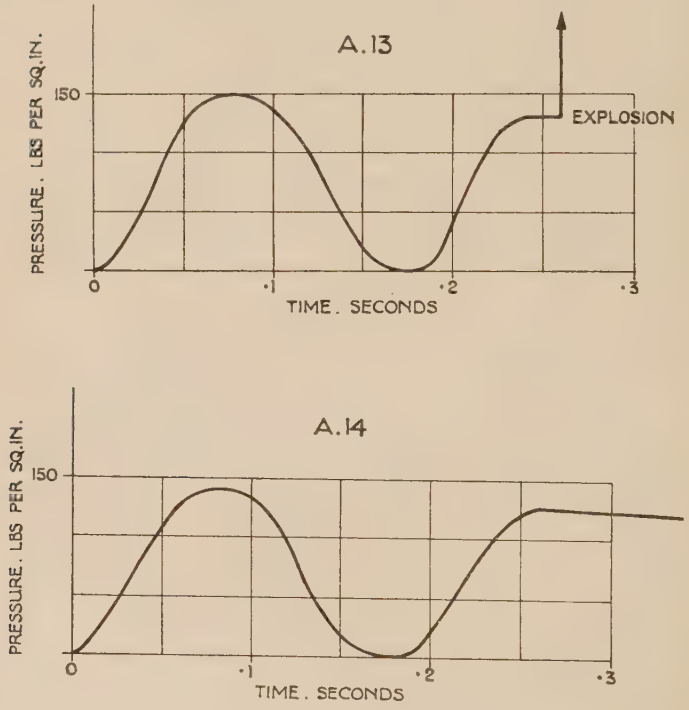
Non-igniting records.			Records on which explosion subsequently occurred.		
1st 1/10″.	2nd 1/10″.	1st 1/5″.	1st 1/10″.	2nd 1/10″.	1st 1/5″.
8·5	6·9	15·4	5·3	5·6	10·9
8·9	7·7	16·6	10·9	7·3	18·2
9·7	6·5	16·2	11·3	7·3	18·6
9·3	5·7	15·0	9·7	6·1	15·8
			8·9	6·5	15·4
	Mean	15·8	11·3	6·5	17·8
			13·3	4·9	18·2
			8·9	7·7	16·6
				Mean	16·6

It will be observed that the average rate of fall of pressure during 1/5th of a second after compression is the same, within the limits of experimental error, whether the

mixture subsequently ignited or not. The actual amount of heat generated by combustion during the delay periods must, therefore, have been negligibly small.

Two other experiments with mixtures of ether and air are of especial interest in this connexion. In these experiments the clip of the machine which should hold the piston fixed at the end of compression failed to work. Instead of being subjected to a single compression, the mixture was alternately compressed and expanded, and only on the second compression was the piston locked in place. The records appear as fig. 5. In A. 13 ignition occurred,

Fig. 5.



in A. 14 it did not. The initial temperatures were the same in each case, but there was a greater proportion of ether in the mixture used in A. 14. The specific heat was therefore higher, and the average temperature reached on the first compression lower. But the average temperature reached after the second compression of A. 13 is lower than that after the first compression of A. 14, owing

to the loss of heat caused by the two compressions. The fact that the mixture nevertheless ignited is most easily explained on the assumption that, in spite of the low average temperature, a small portion of the mixture reached a considerably higher temperature on the second compression.

6. These observations on the rate of fall of pressure during the delay period are in agreement with Dixon's photographs, and lead to the conclusion that ignition does not occur simultaneously throughout the gas. Our own experiments go further, in that they show that ignition can occur even when the main body of the gas has cooled down to a temperature very far below the average temperature immediately after compression. Hence it is clear that as a rule ignition is initiated by quite a small portion of the gas; and the question at once arises whether the quantitative results on the delay to be expected under different conditions, and on the temperature coefficients of the gas reactions derived by the method indicated in our previous paper, can be justified. The main point at issue is the rate at which the portion of the gas which is going to ignite first is losing heat, and the theory as developed assumes that it is losing heat at the same rate as the average rate for the whole gas. This cannot be strictly true, and therefore the conclusions which rest on such an assumption equally cannot be strictly true. But, nevertheless, the rate at which the nucleus of combustion is losing heat must bear some relation with the average rate—that is to say, it must increase when the average rate increases,—and therefore we should have no hesitation in accepting the quantitative results as relatively true. This is borne out by further experiments, which show how closely the observed ignition temperatures of the substances dealt with agree with the observed temperatures in the old and larger apparatus when the difference in the rate of loss of heat, which is considerable, is taken into account.

7. For this purpose it was first necessary to compare the rates of loss of heat after compression in the new and old apparatus. It was shown in the previous paper that the rate of loss of heat was practically proportional to the difference between the average temperature of the gas and the temperature of the water, and could therefore be expressed by the equation

$$-\frac{d\theta}{dt} = \alpha(\theta - \mathrm{T}),$$

θ being the gas temperature and T the wall temperature.

It was shown that the factor α was not quite constant, as the gas temperature fell, but nearly so, particularly when the specific heat of the gas was high *. The effect of running the fan in the combustion space was to increase the cooling factor α about two to three times.

In the present series of experiments both time and pressures could be measured with greater accuracy than previously, and the records gave regularly varying values of α as shown in the following Table II., where results are given for cooling curves after compression in the ratio of 6 : 1 of air and hydrogen, with and without the stirring fan in action.

TABLE II.

Cooling Factor, α.

Time interval from moment of maximum pressure.	Air.		Hydrogen.	
	Without fan.	With fan.	Without fan.	With fan.
·05	1·43	2·72	3·13	6·0
·1	1·27	2·44	3·06	5·4
·15	1·20	2·30	2·80	4·9
·2	1·10	2·21	2·67	4·55
·3	1·02	2·11	2·43	4·00
·4	·95	2·00	2·20	3·57
·5	·89	1·90	2·04	3·27
·75	·805	1·70	1·7	2·74
1·0	·765	1·62	1·65	2·40

These figures show in the first place that the rate of heat loss is by no means proportional to $(\theta - T)$, and a comparison of the results with and without the fan seems to show that the falling off with time of values of α is not due to the dying down of turbulence in the cylinder, since both with and without the fan the value of α falls in roughly the same ratio during the first second.

A comparison with values of the cooling factor given in the previous paper † and obtained on the earlier machine shows that the new machine gives in all cases considerably higher values. The earlier figure for the cooling factor of air without the fan at 6 : 1 compression was about 0·76. Rather higher values would be expected with the new machine, owing to the combustion space having a greater ratio of surface to volume.

* Compare Tables I. and IV , Phil. Mag. July 1922, pp. 92 & 101.

† *Loc. cit.*

8. Table III. gives the results of typical experiments by which the behaviour of mixtures of ether and air on compression in the old and new apparatus can be compared. The results with the old apparatus are quoted from the previous paper.

TABLE III.

	Compression ratio.	Initial temperature.	Delay before ignition.	Cooling factor.
Old apparatus without fan.	4·83	24° C.	No ignition.	0·47
	5·02	23° C.	0·41 sec.	—
Old apparatus with fan.	5·73	24° C.	No ignition.	1·28
	5·94	22° C.	0·13 sec.	—
New apparatus without fan.	6·09	24° C.	No ignition.	1·3
	6·09	24° C.	0·11 sec.	—

In the first of the two quoted experiments with the new apparatus, the amount of ether present in the mixture was greater than in the second. Owing to the higher specific heat of the mixture, the compression temperature is lower. This accounts for the fact that no ignition took place, although it occurred in the second experiment quoted. In this experiment the strength of the mixture was practically the same as in the experiments with the old apparatus. The cooling factor was calculated from the rate of fall of pressure after compression in the first experiment. The figure given is the average over the first 0·3 second after compression. It is practically the same as the cooling factor calculated for the old apparatus when the fan was running. It will be noticed that the compression ratios necessary to cause ignition under these conditions are practically the same, and were very considerably higher than the compression ratio necessary to cause ignition in the old apparatus when the fan was not running and the rate of cooling after compression was only about one-third as great.

9. Similar results obtained with mixtures of heptane and air are shown in Table IV.

TABLE IV.

	Compression ratio.	Initial temperature.	Observed compression pressure.	Calculated average compression temperature.	Delay before ignition.	Cooling factor.
Old apparatus without fan.	5·55	51° C.	141	280° C.	No ignition.	0·49
	6·56	35° C.	176	282° C.	0·58 sec.	—
Old apparatus with fan.	6·13	59°·5 C.	161	310° C.	No ignition.	1·47
	6·33	59°·5 C.	165	313° C.	0·13 sec.	—
New apparatus without fan.	6·09	64° C.	153	295° C.	No ignition.	1·23
	6·09	66° C.	153	298° C.	0·45 sec.	—

It will be observed that the ignition temperatures and the cooling factors correspond. A more accurate comparison can be made by calculating from the observed ignition temperature in the old apparatus (without fan) what the ignition temperature in the new apparatus should be when the difference in the rate of cooling is taken into account According to the equation developed in the previous paper, the ignition temperatures should be connected by the equation

$$\log \frac{Q_0'}{Q_0} = \frac{b}{T_0}\left(1-\frac{T_0}{T_0'}\right),$$

T_0 and T_0' being the ignition temperatures when the rate of loss of heat is Q_0 and Q_0'.

$$\frac{Q_0'}{Q_0} = \frac{\alpha'(T_0'-\theta')}{\alpha(T_0-\theta)},$$

α, α' being the cooling factors, and θ, θ' the wall temperatures.

Hence, from the figures given above, $\frac{Q_0'}{Q_0} = 2{\cdot}6$ approx.

The factor "b" corresponds to the temperature coefficient of the reaction, and was obtained by measuring the length of the delays before ignition at different temperatures. It was shown that $b/T_0 = 10$.

Hence

$$\frac{T_0}{T_0'} = 1-\tfrac{1}{10}\log\frac{Q_0'}{Q_0}$$
$$= {\cdot}96,$$
$$T_0' = \frac{553}{{\cdot}96} = 577 = 304^\circ\,\mathrm{C}.$$

The actual observed temperature of ignition was 298° C. The agreement is therefore good.

10. These experiments, and many other experiments we have made with substances of the same type which are liquid at the ordinary temperatures, lead to the general conclusion that the ignition of such substances can be quantitatively explained on the simple thermal theory that the reaction between the compounds and oxygen proceeds at a rate which is conditioned by temperature, and that ignition or non-ignition depends on the rate of loss of heat at this temperature. If the rate of loss of heat is measured, the ignition temperature under one set of conditions can be calculated from the observed ignition temperature under other conditions. The consistency of behaviour of such

substances is marked ; ignition always occurs if the limiting temperature is reached on compression. When mixtures of ignitable *gases* and air are similarly compressed we do not find such consistency ; and temperature and rate of loss of heat do not seem sufficient to account for the phenomena observed. The results of experiments on hydrogen and acetylene will be given in another paper.

11. For the sake of completeness, Table V. contains the chief results of a large number of experiments with pure pentane, hexane, heptane, and octane. With the exception of heptane, the pure specimens were kindly lent to us by Professor Sydney Young. In all these experiments the compression ratio was 6·09 : 1, the compression temperature being controlled by varying the initial temperature.

Table V.

Substance.	Initial temperature.	Minimum "average" temperature of compression to produce ignition.
Pentane.....	91·5 (90·5)	316° C.
Hexane	78 (77)	307° C.
Heptane.....	66 (64)	298° C.
Octane	60·5 (59)	297° C.

The figures in brackets show the initial temperatures in experiments when ignition did not occur on compression. The "average" self-ignition temperatures are calculated from the observed compression pressures. Owing to absence of any accurate data on the mean specific heats of the vapours over the range from the initial temperature to the compression temperature, it is impossible to calculate accurately the corresponding "adiabatic" ignition temperatures ; but from the approximate calculation made in paragraph 19 of the previous paper it may be concluded that the temperatures of adiabatic compression are not more than 50° C. above the average temperatures given above.

The rates of cooling after compression are practically the same for all these substances. The cooling factor is approximately 1·3. It will be noticed that these experiments show that the ignition temperatures of the paraffin hydrocarbons decrease as the molecular weights increase. This is in agreement with the observation that paraffin hydrocarbons tend to "detonate" more easily in internal combustion engines, the higher their boiling-points.

C. *Time and Chance.* *By* Norman Campbell, *Sc.D.**

Summary.

Very general considerations indicate that a revision of classical conceptions of time is necessary. The view is suggested that time is a statistical conception; that while individual neighbouring events have a definite time-order, any temporal magnitude, such as velocity, interval, or frequency, is significant only with regard to statistical aggregates, and represents a probability of transition characteristic of the individual elements.

The bearing of this suggestion upon outstanding problems is considered:—(*a*) The lack of "reciprocity" in the interaction of an atom and charged particle (Bohr): (*b*) the interaction between matter and radiation, and the conflict between quantum and wave theory; (*c*) quantum mechanics, with special reference to the work of Heisenberg. In no case is any definite theory offered; but it is argued that a theory on these lines must be physically possible, while the mathematical possibility can be discussed only by those more skilled in analysis.

Introduction.

In a letter to 'Nature' a few years ago† it was suggested that the difficulties of reconciling classical and quantum theories might arise from the introduction into the latter of temporal conceptions derived from the former, and that apparent inconsistencies entered because "time" has no meaning within the atom. No attempt to develop this suggestion has been made either by myself or by others, though Bohr ‡ in his recent papers has hinted (of course quite independently) that any formulation of quantum principles in terms of time and space may be impossible. But I venture to raise the matter again, not because I have any definite timeless theory to propose, but because it seems to me that one feature of Heisenberg's § most attractive attempt to formulate a quantum mechanics has been accepted without as much consideration as it deserves.

Heisenberg starts with the determination to include for his formulation only those quantities that are "principiell beobachtbar" ‖. Among the quantities which he takes as

* Communicated by the Author.

† N. R. Campbell, 'Nature,' cvii. p. 170 (1921).

‡ N. Bohr, *Zeit. f. Phys.* xxxiv. p. 142 (1925).

§ W. Heisenberg, *Zeit. f. Phys.* xxxiii. p. 879 (1925).

‖ Born & Jordan (*Zeit. f. Phys.* xxxiv. p. 858, 1925) replace "principiell beobachtbar" by "wirklich augemessen." Of course the objections apply quite as strongly to the second phrase.

satisfying his criterion is $\nu(mn)$, the frequency of radiation emitted associated with the transition from a stationary state m to a stationary state n.

It is dangerous to deny any proposition involving such an exceedingly ambiguous adverb; but it is by no means obvious that if a distinction is to be made between quantities that are observed and those that are not, the frequency of radiation falls into the former class. For determinations of that quantity involve experiments of two totally different kinds: first, interference experiments in which no temporal magnitude is measured nor any change with time observed; second, experiments on the velocity of light in which temporal magnitudes are observed, associated, not with any atomic systems or any changes to which quantum principles would be expected to apply, but with gross material bodies, such as planets or revolving mirrors. Now, as the whole question at issue is why principles which apply to these gross material bodies do not apply to individual atoms or the radiation which they emit, it is surely stretching the meaning of a very accommodating word beyond its elastic limit to say that we have observed "in principle" the frequency belonging to the latter when we have only actually measured a frequency belonging to the former.

Heisenberg, in fact, assumes that all our classical conceptions of time can be transferred without alteration to atomic systems. This is precisely the proposition which seems to me highly dubitable. We shall consider later whether it is really essential to his theory; first it will be convenient to consider an alternative. The view I want to suggest here is that time, like temperature, is a purely statistical conception, having no meaning except as applied to statistical aggregates; that a temporal magnitude, such as an interval or a frequency, is a statistical magnitude and that there is no such thing as the frequency of an atomic change or the interval between atomic events; that time and chance are merely two aspects of the same thing; and that the ultimate magnitude, the statistical average of which is a temporal magnitude, is the probability of a change or (with a slightly more definite connotation) of a transition.

Outline of the Theory.

At the risk of being dubbed metaphysical, perhaps I may start from (but discuss very briefly) the considerations which first forced the idea on my attention, although they are much deeper and are much more general than the particular

problems of quantum theory. They arise when we inquire on what evidence we assert our knowledge of any "routine": that is to say, a collection of invariably associated events invariably ordered in time, such as that described by the law that a body falls with uniform acceleration. In order that a routine may be established, several examples of it must be observed; repetition involves separation in time: the examples must themselves have a time-order. The routines actually observed must have beginnings and ends: and though the internal time-relations of all events in the routine may be the same, the routines are distinguished by the relations of their terminations. What justification have we, then, for asserting that the various examples of the routines are the same, that there is repetition, and that this repetition establishes the routine?

The answer is, I think, that what we profess to establish in such cases is a numerical law of a certain form, which is obeyed by all examples of the routine. This law is valid over an infinite range so long as the conditions which determine it are unaltered. Routines are infinitely extended and have no terminations; the terminations actually observed are not parts of the routine, but represent the intrusion of something that is not a routine. This disturbing element, if it is not of a nature necessarily inaccessible to science, is chance: if we are to give any account at all of the actual terminations observed, we must say that they are due to chance.

That is a very summary account of a very difficult problem. The point I want to make is that time and chance are inevitably associated, because we cannot give any adequate account of routines (on which depend all temporal magnitudes) without recognizing also the influence of chance. We must regard changes in time as of two kinds, the regular kind which can be grouped into routines, and the irregular kind which are due to pure chance; there is no evidence for the former unless at the same time we admit the existence of the latter. The suggestion that we are considering, that time is merely statistical, is simply a proposal for abandoning the first kind of change and for effecting a great simplification in our ideas by recognizing only one kind of time change, namely that due to chance.

The proposal receives strong support from the most fundamental proposition of Einstein's formulation of quantum principles. Chance enters in determining transitions between stationary states. But stationary states are stationary; they represent the absence of all change and therefore the absence of everything to which the concept of time can be

applicable. Chance does not initiate routines, as in the dualistic view which has been generally accepted; it initiates only the absence of change. Changes in time are all changes by chance: there is no such thing as a routine in systems to which quantum principles are applicable.

In the study of radioactivity (to which, as Rosseland has insisted *, quantum principles must be applicable) we have actual experimental knowledge of such a state of affairs. There is no routine whatsoever describing the disintegration of a single atom; it undergoes changes by pure chance, and in the interval between changes by chance nothing whatsoever happens. In fact, the very use of the word "interval" introduces ideas that are really foreign to the facts. If we were really observing a single atom only and had no experience other than that derived from this atom, we could only say that the successive changes occurred in a certain time-order, and that one of these changes occurred in the interval between its predecessor and successor. There could be no question of an interval between successive changes: that would only arise if we observed a second atom and noticed its changes occurring between those of the first atom. But though by such comparison of two atoms we might arrive at the conception of an interval between changes, we could not possibly arrive at a measure of that interval: for in successive repetitions of the comparison the changes in one atom would not occur in the same places in the time-order of the other, still less would the more complex conditions be fulfilled that are demanded for the measurement of periods †.

Measurement of intervals is possible only when large collections of atoms are observed: actually we could use considerable masses of radioactive substances as clocks. The exact details of the process need not be described, but it is important to make sure that the proposition on which it ultimately depends can be stated in statistical terms without the introduction of temporal concepts (other than that of temporal order) applicable to the individual atoms. The proposition is this. Let there be a very large number N of atoms A and a very large number M of atoms B. Let n changes in A be observed and m in B, these changes being such that all the n changes (and no other changes of this type) occur between the first and last of the m changes, or *vice versâ*. Then it is an experimental fact that, if n and m are increased indefinitely, while the ratios $n : N$ and $n : M$ are

* S. Rosseland, *Zeit. f. Phys.* xiv. p. 173 (1923).

† The conditions necessary for the measurement of periods are discussed in the appendix to my 'Physics' (Camb. Univ. Press, 1922).

decreased indefinitely, the ratio n/m tends to a limit characteristic of the atoms A and B and the type of change in them observed. This proposition enables us to measure magnitudes having the properties associated with periods; but it is a purely statistical proposition, having no meaning as applied to individual atoms. The view that is suggested here is that all clocks are essentially similar to radioactive clocks and depend on similar statistical propositions.

The value of these ideas would be proved decisively if it were possible to produce a theory, involving no temporal conceptions other than time-order, which would reduce all quantum phenomena to a few simple principles and at the same time to show that all the experiments on which the prevailing temporal conceptions are based can be described adequately in terms of statistics. I make no pretence of being able to achieve this aim even approximately; and so long as it is not achieved, there is a certain difficulty in considering the ideas at all. Temporal conceptions are so deeply embedded in all our thoughts and language that, if we decided to abandon them entirely in discussing atomic phenomena, we should find that we could not even state adequately the problems we desire to solve. This is, of course, no objection to our theory, but a point in its favour; but a mere denial that certain questions which have troubled us are significant cannot be regarded as a complete solution of an inconsistency unless something positive is added to our thought to replace that subtracted from it. While the complete solution is lacking, it will be wiser to abandon all attempts at formal consistency, and to use temporal conceptions freely, even in circumstances in which their validity is denied, if by so doing we can hope to arrive at suggestions in what direction to seek the complete solution.

Thus, strictly speaking, we deny that there is such a thing as the interval between two successive transitions in a single individual system, or that there can be any meaning in a proposition asserting that any one such interval is equal to or greater than another. But it is more convenient, so long as we recognize the danger of misinterpretation, to admit the conception of the interval and the ideal possibility of measuring it, but to assert at the same time that this interval is wholly irregular, so that no law, other than a statistical law, can be asserted of it. With this preliminary explanation, let us turn to a few of the outstanding problems of quantum theory.

Interaction of Rays with Atoms.

The easiest to resolve is that which Bohr * has indicated recently in connexion with the interaction between atoms and charged particles. The lack of "reciprocity" arises when the time that the interaction lasts is short compared with the period characteristic of the atom. The conclusion that it is short depends entirely on the assumption that the motion of the particle and the oscillation of the atom are "uniform." This, of course, we deny. Particles moving with "uniform" velocity or oscillating in fixed orbits are, in our view, undergoing fortuitous transitions between the points of their paths, the intervals between these transitions being wholly irregular, but possessing a statistical average related simply to the distance covered in the transition. Sometimes the time during which the atomic electron and the ray are near enough to interact is long, sometimes it is short; sometimes they will disturb each other much, sometimes very little. It follows that the only characteristic of an individual particle, inside or outside the atom, is its path, the locus of the points between which transitions occur; its velocity, its kinetic energy, the magnetic field it exerts are all statistical magnitudes, characteristic not of single particles at a single instant, but only of large aggregates of particles or (possibly) of a single atom observed at a large number of instants. And, as a matter of fact, the path of an individual ray is all that ever has been observed, or is likely to be observed. Unless we can measure, by the methods from which these quantities derive their meaning, times of the order of 10^{-12} sec. or energies of the order of 10^{-12} calories, no experiment can contradict our hypothesis.

Radiation.

But does it help us to overcome the great difficulty of radiation, and to reconcile the quantum and wave theories? Not, of course, without some modification of both, but the necessary modifications seem a natural consequence of it. At the outset we deny that radiation is periodic in time at all. We accept the direct experimental datum that atomic transitions result in the establishment of an electromagnetic field (by which we mean a modified probability of transition of atoms immersed in it) periodic in space about those atoms; but we deny the periodicity in time. As a consequence we can deny also the permanence of this field, for it no longer has to endure in order to produce its effect.

* N. Bohr, *loc. cit.*

We suppose that the transition from a path of a higher to one of lower mean energy, which "emits radiation," establishes immediately round the atom the field periodic in space; an electron in the field at the lower level acquires an increased probability of transition to a higher and, in virtue of this probability, there is established around it a secondary field periodic in space (which it is natural to regard as opposite in sign to the first). The various secondary fields, superimposed on each other, interfere like Huyghens wavelets, and produce a periodicity on a larger scale which we detect by our instruments. As soon as the compensating transition takes place, after an interval and at a point determined by the probabilities established by the field, the fields vanish.

This picture is obviously similar to that of Bohr, Kramers, and Slater. But it has the advantage of not being disproved by the experiment of Bothe and Geiger *. That experiment showed that the time-interval between the emitting transition and the consequent ionization of another atom is short compared with the average interval between succession ionizations. But this result raises a difficulty only if it is assumed that the radiation endures for the whole interval between successive ionizations. This we deny; all that the experiment proves for us is that the time for which the radiation endures is something less than 1/1000 sec.; it would clearly be surprising, in our view, if it lasted as long. Incidentally, it may be noted that we may get a very simple explanation (which never seems to me to be afforded satisfactorily by the classical theory) of why light from different sources does not interfere; it may be simply because the chance that the radiation fields from the two sources are actually present at the same time is infinitesimal.

It may be said that this is no explanation, for it involves the abandonment of the wave theory; in particular it leaves no room for a finite speed of propagation of light. The first part of this statement may be admitted, for any acceptance of quantum theory involves such abandonment. Maxwell's equations (one of which is a generalization of Ampère's law) apply in the first instance to material systems, made up of electrons moving in electric and magnetic fields, to which quantum principles must ultimately apply. Any argument which professes to deduce from these equations any proposition about a radiation continuous in time and space, and therefore outside those principles, must contain either a fallacy or a concealed assumption concerning the relation

* W. Bothe and H. Geiger, *Zeit. f. Phys.* xxxii. p. 639 (1925).

between continuous and discontinuous phenomena. There is no inconsistency in combining a wave theory with the quantum theory, but there is inconsistency in asserting that this wave theory can be deduced from Maxwell's equations in their present form.

But the second objection cannot be admitted; there is clearly room for an explanation, so long as the explanation is sought in the right direction, which is the opposite to the usual direction.

The quantity c enters into physics in two ways: first as the velocity of light, second as the ratio of a magnetic to an electric force. Maxwell's theory takes its second significance as fundamental, and seeks to explain the first. But relativity clearly tells us that we must reverse the process. The so-called velocity of light is the ultimate universal constant of all physics. It does not, of course, represent a velocity in our sense, that is to say the probability of transitions along a path; it represents the invalidity of the conception of simultaneity for events which are separated in space. There is no such thing as the simultaneity of two events that are not neighbouring, and we must avoid that conception even in stating the facts from which we measure c. We must describe those facts by saying that if A is a transition associated with a transition B in a distant system in the manner of which the statistical representation is cause and effect, and if B is similarly associated with C in a system neighbouring to A, then C is not statistically simultaneous with A but is later *, the statistical interval being proportional to the distance of A from B. That experimental fact we take as ultimate and inexplicable.

Now consider a particle moving in an orbit, or, as we say, undergoing transitions the locus of which is a closed curve. Each of these transitions is associated with that immediately preceding in the manner described; and consequently, since the path is closed, a transition at P is associated, through an intermediate chain, with itself; speaking conventionally, the stimulus returns on itself. If the path were infinitely small, the return stimulus would be statistically simultaneous with the outgoing stimulus; but if the path is finite it will be later. The probability of a transition at any point, being determined partly by the return of the stimulus which the transition sets up, will thus be affected by the dimensions of the closed path. But the statement that the force on a particle is changed is the statistical representation of the

* Or earlier; the decision between the two alternatives depends on a mere convention concerning the sign of the causal relation.

assertion that the probability of its transitions is changed; consequently the force on the particle (and the force which it exerts on other particles) will depend on the dimensions of the path and, probably, on the probability of transitions in it as compared with that in other paths of the same size. That is to say, the (electrostatic) force which the particle would exert and experience if it were not undergoing transitions will be modified by another (magnetic) force depending on the size and velocity of the orbit. Whether it is possible by any mathematical argument based on these ideas to establish the necessary relation between the form of the orbit, the statistical velocity, the quantity c, and the magnetic force is a matter on which I offer no opinion. But such an argument is physically conceivable.

Quantum Mechanics.

Finally there is the problem of quantum mechanics. Does the conception of a statistical time enable us to understand better why stationary states are discrete and differ by finite amounts of energy, or how the energies characteristic of them depend on the constitution of the system? It is clear at once that a mere alteration of our ideas of time imposed upon classical theory will not explain everything; the existence of the universal constant h, which is not a purely temporal constant, necessitates the introduction of some new ideas that are not temporal. The best that we can hope to do in explaining this constant is to exhibit a connexion between the two aspects under which h appears, determining first the stationary states that are possible and secondly the character of the radiation associated with transitions between them.

It seems to me that the views just discussed do help us to understand this connexion; for we regard the stationary states as consisting of transitions just as much as the changes from one stationary state to another; the only difference is that, while these changes consist of transitions between states of different mean energy, the stationary states consist of transitions between states of the same mean energy. If h is connected with one kind of transition, we should expect it also to be connected with the other. Further, on our view the periodic field which appears experimentally as radiation is not consequent on a transition between stationary states and separable from it, at least in conception; it is simply the expression of the existence of a certain probability of transition. Planck's formula states a relation,

which must be regarded as ultimate and inexplicable, between the spatial periodicity of the field and the change of energy in the transition the probability of which is expressed by the field. In a stationary state, where there is no probability of change from that state, there is no probability of change of energy; the periodicity is infinite; the field is aperiodic. When there is a probability of a transition between stationary states with change of energy, the periodicity is finite; there is radiation. It must be clearly understood that the frequency of radiation, a temporal magnitude measured by the ratio of c to the wave-length, is not the statistical frequency determined by the probability of transition. The two are related in so far as the probability of transition is related to the energy change involved in the transition. In a single system the relation is doubtless unique, so that the frequency of radiation is a single-valued function of the statistical frequency of transition; but it is not impossible that in two different systems transitions could be found with the same probability and the same statistical frequency and yet of different energy change and therefore with different frequencies of radiation. The further study of the relation between frequency of radiation and statistical frequencies of transition (which, of course, is fundamental in Einstein's theory of complete radiation) seems highly desirable; for both these quantities are accessible to experiment.

These suggestions appear to be in accord, so far as accord is possible, with the quantum mechanics of Heisenberg and of Born and Jordan. For they, too, seem to regard stationary states as consisting of transitions. Their analysis depends on the use of double-affix quantities, such as $\nu(mn)$, which are associated with transitions, and in the formal treatment they make no essential distinction between quantities in which the affixes are different and those in which they are the same; but these latter can be associated only with transitions within the same stationary state. They actually represent the energy of a stationary state by a diagonal matrix with two similar affixes, $\mathrm{H}(nn)$.

But this is as far as we can go in establishing a relation between our ideas and Heisenberg's theory; for there is a fundamental incompatibility between them. We are aiming at a physical interpretation, an interpretation in terms of concepts that are based as firmly as possible on experimental facts. Heisenberg's theory in its present form is not capable of any physical interpretation at all. It aims at deducing from a Hamiltonian equation of any form the energy of the

stationary states of a system to which that equation is applicable. But the very form of the deduction involves a denial that a Hamiltonian equation of any form is really applicable to the system; it denies the assumption, which underlies all classical dynamics, that the state of a system can be expressed by a series of one-one relations between space and time. To admit this is not to deny that the theory may be of great value; it may provide the best or the only mathematical analysis whereby certain physical truths can be revealed. And perhaps an inconsistency of this kind does not trouble mathematicians; indeed, a study of their excursions in relativity strongly suggests that it does not *.

But the inconsistency must be removed before there can be any physical interpretation. It would be abolished if it were possible to dismiss altogether the conception of time, and start, not from a Hamiltonian equation involving time, but from a relation between the quantities which determine the constitution of a system to which, according to classical theory but not according to quantum theory, the Hamiltonian equation is applicable. In place of talking about a harmonic oscillator, we must talk about (*e. g.*) an electron inside a uniform positive sphere. Again, I do not profess to know whether the essentials of the Heisenberg calculus could be preserved in this change; but it is not inconceivable that they might be. For instance, we might still have the same formal equation on which the calculus is built—

$$\nu(mn) = \nu(mk) + \nu(kn);$$

but the ν's would now have a different physical significance. At present they are frequencies of radiation, and the difficulty arises at once that this equation, which states that frequencies are truly additive, like fundamental magnitudes, cannot be true generally of frequencies. Periods are, but frequencies are not, fundamental magnitudes in this sense. On the other

* It is curious that they take it so lightly. For the prevalent school of mathematician-philosophers regard internal consistency as the prime criterion of truth. It seems that the deduction of conclusions which render insignificant the concepts of the premisses is an indication of falsity only if these concepts are purely mathematical; if they derive any part of their significance from sense-perception, the inconsistency does not matter. In simpler words, it is impossible to talk nonsense about what you know directly; and while you must not say that even numbers are odd, you are a true mathematician and display gloriously your freedom from the prejudices of the hide-bound physicist, if you assert firmly that black cats are white. I do not know that this doctrine has ever been formally maintained; I have merely deduced it from current practice.

hand, there are circumstances of great generality in which probabilities are additive, and others in which the logarithms of probabilities are additive. If, in the revised calculus, the v's turned out to be probabilities or their logarithms, we might at once have a physical interpretation, and see an ultimate reason why mean energies are discrete and additive, and why the most fundamental proposition of quantum theory is true.

In conclusion, some apology seems to be needed for offering such a collection of incomplete and incoherent suggestions. If anyone can make any use of them he will be much better entitled than myself to be regarded as their author.

Feb. 18, 1926.

CI. *A Thermionic Valve Method of measuring the Velocity of Air-currents of Low Velocity in Pipes.* *By* J. A. C. Teegan, *M.Sc.**

[Plate XVIII.]

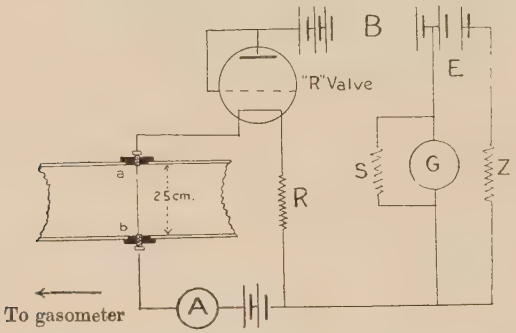
THE fact that a fine platinum wire heated electrically undergoes a change in resistance due to cooling when immersed in a stream of fluid, has been utilized as a method of practical anemometry. Hot-wire anemometers based upon this principle have been described by Morris, and later by Thomas, who first applied them to the measurement of the velocity of fluids in pipes. The designs favoured by these workers resemble a bolometer arrangement, the cooling produced by a stream of fluid causing a change in resistance of a fine platinum wire which composes one arm of a Wheatstone bridge. In this paper a hot-wire anemometer of quite a new type is described, which has been found quite satisfactory for the measurement of slow-moving streams of air in pipes.

Into the filament circuit of an ordinary R-type thermionic valve a fine platinum wire (2·5 cm. long and 0·010 cm. diameter) was placed. This wire was stretched across a cylindrical tube 5 ft. long and 2·5 cm. diameter. The method of inserting the wire is indicated in fig. 1. The ends, a, b, of the wire were affixed by the smallest possible amount of solder to two brass screws fixed diametrically with respect to the section of the tube. Two stout insulated copper wires were attached to these screws, and were connected, as indicated, into the filament circuit of the valve, which also

* Communicated by John J. Dowling, M.A., F.Inst.P.

contained a reliable ammeter A and rheostat R (fig. 1). The tube containing the platinum wire was clamped horizontally, and was securely connected by a pipe, of the same diameter, to a gasometer of 8 cubic feet capacity. The gasometer was fitted with ball-bearing pulleys, and its rate of fall was found to be exceedingly uniform, so that quite small air-streams could be produced and measured with accuracy.

Fig. 1.

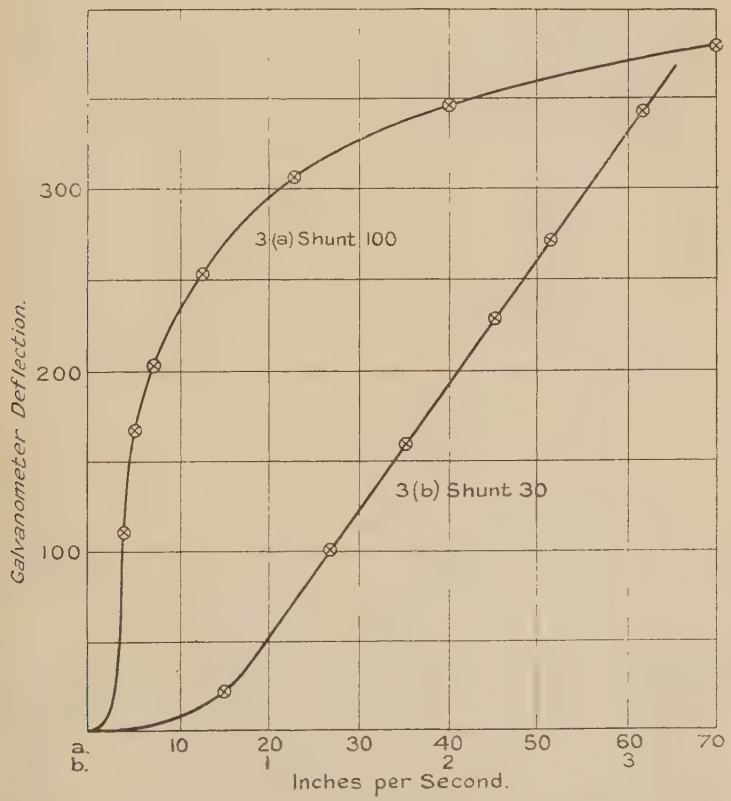


When a stream of air cools the platinum wire, its resistance diminishes, and a greater p.d. is therefore applied to the valve filament. The resulting increase of filament temperature causes a corresponding increase in the current flowing in the anode circuit BG. The anode-current variations can be utilized as a measure of the velocity of the air-stream passing the wire. The grid and anode were joined and sufficient voltage applied for saturation. To enable a sensitive galvanometer to be used, a "zero-shunt" arrangement is employed. It is represented in fig. 1, and consists of a few cells E (6 volts) in series with a resistance Z, the whole being in parallel with the galvanometer G. If I is any value of the anode current, a current $\frac{Z}{Z+G}(I-I_0)$ passes through the galvanometer branch, where $I_0=\frac{E}{Z}$ and G is the galvanometer resistance. Thus, for valves of anode current in the neighbourhood of I_0 a galvanometer of high sensitivity can be used to measure slight deviations from the standard value I_0. The galvanometer used in these experiments had a sensitivity of 300 scale-divisions per micro-amp.

In determining a suitable value of heating currents for the measurement of comparatively low velocities of flow,

the presence of the free convection current is of considerable importance. The wire being mounted horizontally, this convection current is at right angles to the cooling stream. The effective velocity of the cooling stream is $\sqrt{V^2 + v_c^2}$, where v_c is the velocity of the convection current, and V is that of the impressed air-stream. It is evident that v_c will diminish as V increases, since an increase in V lowers the temperature of the wire. If the diminution in v_c is proportional to V or to V^n (where n is a positive integer),

Fig. 2.



then the free convection current will have less influence on the form of the calibration curve the lower the heating current employed. A filament current of 0·6 amp. was used in this work, further reduction being found unsuitable, owing to the curvature of the valve emission curve commencing in the vicinity of a filament current of ·55 amp.

Fig. 2 (*a*) shows the relation between galvanometer deflexions and velocity of the air-stream (in inches per sec.). Over a range of velocities from ·7 inch per sec. to 5 inches per sec. the calibration curve is practically linear. The effect of the free convection current is clearly shown at the lower end of the curve. The sensitivity is quite good, equal to that obtained by other workers, and the readings are quite steady.

It was not generally possible to increase the sensitivity by lowering the galvanometer shunt ($\times 30$) as the readings showed unsteadiness. It is possible that, with a better constructed flow-tube, in which sources of error due to cooling effects of the leads etc. were more completely eliminated, the sensitivity would be increased tenfold. In fig. 2 (*b*) the calibration curve for higher velocities is shown. It resembles that obtained by other workers.

Over a considerable range of velocities a fairly open scale of deflexions is obtained. As the velocity is increased, a point is reached where the curve turns over. The range could be extended to the higher velocities by increasing the temperature or diameter of the wire ; using either a power value or a number of values in parallel. Since the anode current employed when using a valve in this way is large, it is necessary to use H.T. batteries of large capacity. A battery built up from a number of separate cells was found most satisfactory, the steadiness of the readings of the anemometer being very much improved.

An interesting test was made with this apparatus on the occasion of the second explosion test at La Courtine, the apparatus not having been ready in time for the first. The platinum wire was mounted in a short tube leading into an empty steel cylinder of about 80 litres capacity. A second galvanometer, in series with the first, recorded on a moving kinema film. The apparatus was run continuously for an hour covering the time at which the explosion wave might have been expected to arrive in Dublin. Plate XVIII. represents a portion of the resulting record, and the two large deflexions thereon were much larger than any other of the irregular galvanometer movements. We were informed by the Air Ministry, London, that the times indicated agreed pretty well with other long distance records obtained elswhere.

CII. *Evidence of Molecular Changes in Vapours and Liquids.* By G. N. Antonoff, *D.Sc.* (*Manch.*) *.

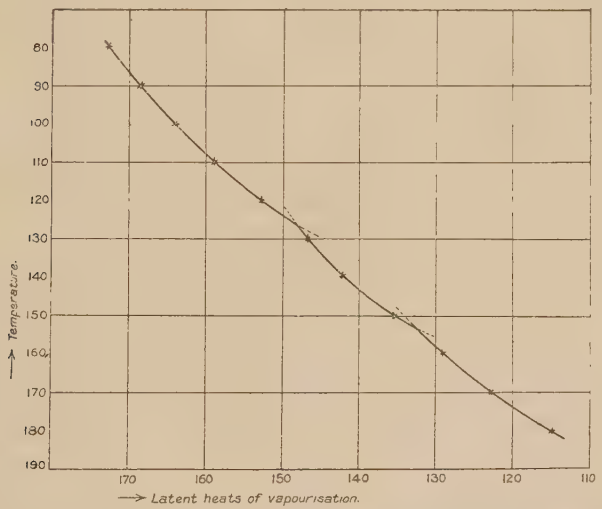
I.

Introduction.

IN my previous paper † I collected evidence indicating that some properties of liquids vary with temperature in a discontinuous manner. Thus, densities, latent heats of vaporization, surface-tensions, and viscosities were found to possess the above character.

The discontinuity of curves representing the variation of latent heat of vaporization with temperature is so conspicuous that one cannot help noticing the same (see fig. 1).

Fig. 1.



In some other cases it is by no means obvious at first sight, and it took me quite a long time to make sure that such is actually the case, and is not a result of imagination. The difficulty is that in most cases one has to deal with changes which do not exceed appreciably the limits of experimental errors. In the case of latent heats (λ) of vaporization, as I said, the effect is much stronger, but it depends upon the

* Communicated by the Author.

† Phil. Mag. vol. l. p. 265, July 1925. In this paper I found a certain number of misprints particularly in the tables. For example, on p. 273 in the first line $\bar{1}$·63000 stands for ·16300, and on p. 272 1·55470 stands for 1·55470; correspondingly on p. 275 first line, 663·0 should be instead of 66·30.

measurement of densities, and therefore cannot be regarded as an independent evidence.

The figures I used were taken from the paper by Sydney Young (Proc. R. Dublin Soc. xii. June 1910), as calculated by Dr. J. E. Mills, by his formula

$$\lambda = \frac{K}{\sqrt[3]{d} - \sqrt[3]{D}},$$

where λ is the internal heat of vaporization, and d and D are densities of liquids and saturated vapour.

Similarly, if λ is calculated from the Clausius-Clapeyron formula

$$\lambda = T\frac{dP}{dT}(V - v),$$

where T is the temperature, V the specific vol. of vapour, v the specific vol. of liquid, and P the vapour-pressure, the discontinuity will be partly due to V and v (the reciprocal values of densities) and partly to P, which is apparently also discontinuous.

These data were of great service to me all the same, as they enabled me to locate the kinks without much labour, simply by plotting them on millimeter paper. However, I fully realize that all depends upon the density curves whether their discontinuity is beyond doubt.

Although the effect in question is small, there is no doubt that the measurements of densities can be carried out with much greater accuracy than those of most of the physical properties. The experimental figures are given with four decimal places, and the discontinuity can be noticed if only three figures are taken into consideration. Although in some individual cases there may be some doubt as to the actual position of a kink, in the majority of cases the results are quite definite.

In my previous paper I gave as an example the results for three substances of a very different chemical character, but I satisfied myself that the same is the case with all other substances for which there are accurate experimental values.

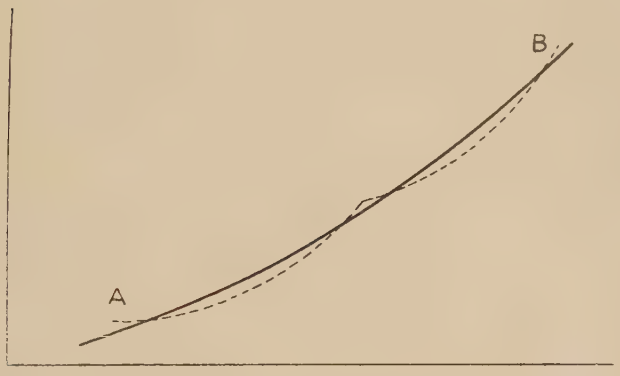
I have not investigated water owing to the want of figures at higher temperatures, and the behaviour of water near 4 C. is the only case so far where the laws outlined in my previous paper do not apply.

Thus, I have no doubt whatever that the above phenomena are real. However, since the publication of my last paper I have been in correspondence with a number of men of science, who criticized my work, and I find it therefore necessary to give some additional explanations.

Thus, for example, an opinion was expressed that such

formulæ as I used for small portions of the density curves can be equally well applied with a sufficient degree of accuracy to a perfectly smooth and continuous curve. As my equations contain three constants they can be always adjusted so as to fit fairly accurately into separate portions of a perfectly continuous curve AB, as in fig. 2.

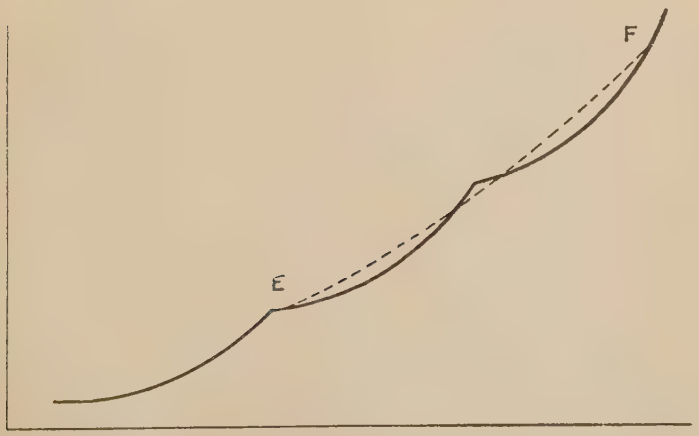
Fig. 2.



My answer to this criticism is as follows :—

If the curve were smooth, an approximate equation could be applied to any small part of the curve, between any two points. Experience has shown me, however, that such is not the case if the curve is discontinuous. Only those parts

Fig. 3.



of the density curves can be fitted accurately into an equation of a smooth curve, which are situated between two kinks.

Fig. 3 represents a density curve in an exaggerated form.

It can be seen that a part of the curve between E and F cannot be forced into an equation of a smooth curve.

It may be interesting to mention that I first discovered these kinks, not by noticing them on a drawing, but by finding that there are definite points on the curve between which only an equation of a smooth curve can be applied. Thus, I found that between these points an exponential expression can be applied with accuracy, the deviations being sometimes of the order $\pm$·0001 or even less.

If, however, I try to apply an equation of a smooth curve between any other points (such as E and F in fig. 3), I find that the deviations become systematic, of a much greater order of magnitude than the above, and, in fact, only the points on which the curve is based will coincide accurately with the experimental results.

Only after these calculations revealed to me the existence of kinks, I plotted the figures on a piece of millimetre paper, on such a scale that 1 mm. corresponded to a unit in the third decimal place. With the use of a flexible steel curve, I drew the curve which revealed the kink on exactly the same places. Between these kinks, and only between them, an equation of a smooth curve could be fitted in accurately.

I thus found that the points nearest to the kink generally contain an appreciable error, which is probably due to interpolation, but apart from that I believe the experimental figures to be accurate within $\pm$·0001, on the whole, *i.e.*, within these limits they can be fitted into a smooth curve as a rule, at least in those regions where the experimental difficulties are not too great. It may be that the actual errors of observation were bigger, but the figures were smoothed afterwards. In such case a curve drawn on the basis of these figures is the best representative line.

In any case the experimental figures indicate the existence of quite a definite physical phenomenon, which cannot be attributed to experimental errors. I can quite imagine that in one case or two the experimental errors might be misleading and indicate the existence of purely imaginary relations, but the fact that these phenomena occur invariably with all liquids, at all temperatures, is a sufficient guarantee of their reality.

I am quite sure that kinks may appear much more distinctly under certain circumstances, and I can think of certain closely-related phenomena governed by precisely similar laws where one can succeed in finding them without much difficulty.

In my previous paper I mentioned that in dealing with

pure liquids I always bore in mind systems capable of separating into two liquid layers, which I generally call systems liquid-liquid, to distinguish them from systems liquid-vapour, *i.e.*, pure liquids in equilibrium with their vapour.

Comparing systems liquid-vapour with systems liquid-liquid, one cannot help noticing a striking similarity. Both systems have a typical critical point, with the typical phenomenon of opalescence in the critical region all round the critical point. In both cases the system separates into two phases of equal volume, in the critical point.

In both systems the meniscus separating the two phases in equilibrium is flat at the critical point and in its vicinity, etc.

The only difference is that in one case the one phase is liquid, the other gaseous, and in the other case both phases are liquid. With this reservation one cannot help seeing a striking resemblance between the two phenomena.

In this paper I shall treat these two categories of phenomena in parallel. By extending the analogy between them one can draw valuable conclusions because properties of one of them often reflect light upon the other. Of all physical properties I am particularly interested in densities and surface-tensions, and I shall deal with them in separate paragraphs. On the other side, I find that certain valuable conclusions as to the structure of liquids can be deduced from the study of conditions of equilibrium, and to this subject I devote two separate sections as well.

§ 1. *Densities.*

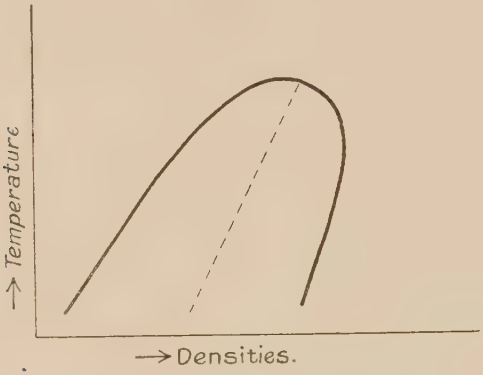
One of the striking examples of similarity between the two systems is the fact that they both follow, as a rule, the so-called Mathias-Cailletet law of rectilinear diameter.

Fig. 4 represents the densities of a liquid and its saturated vapours as a function of temperature.

This curve is, as a rule, of the shape of an asymmetric parabola. It is often observed that the values of $\frac{\delta_l + \delta_v}{2}$ (where δ is density of liquid, and δ_v that of its vapour) fall into a straight line. The intersection of this line with the parabola indicates the position of the critical point. Every horizontal line intersects the two branches of the parabola in points which represent the density of liquid and of its vapour at the given temperature. In my previous paper I dealt with this subject in brief, and there I gave reasons

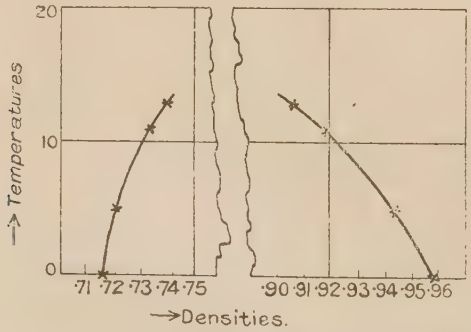
why I believe that this parabola is discontinuous, although to a very small degree. The general character of the curve is such that it certainly does not suggest the idea of discontinuity. Only a very careful examination can reveal it, and even then it is difficult to convince other people who have not gone through the amount of work I have. The effect is so small that it is only slightly above the limits of experimental errors.

Fig. 4.



The same can be said about systems liquid-liquid. I have determined experimentally the densities of coexisting liquid layers for the system aniline-amylene, at different temperatures. (See fig. 5.) The curve appears to be very nearly smooth.

Fig. 5.



In the systems capable of separating into two layers the relation between the specific weights and concentration is by no means simple.

Thus, for aniline and amylene, at 19°·3 C., *i. e.* about 5°

above their critical point of dissolution, I found the relation as represented in fig. 6.

Fig. 6.

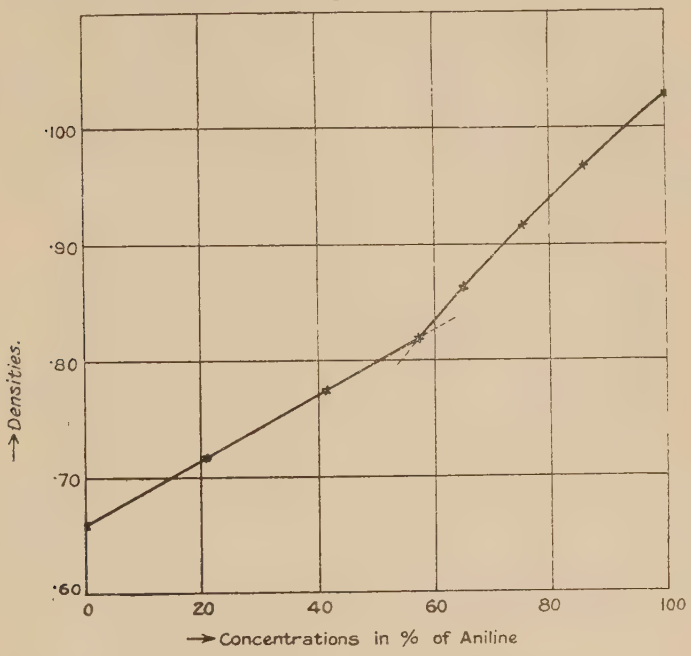


Fig. 7.

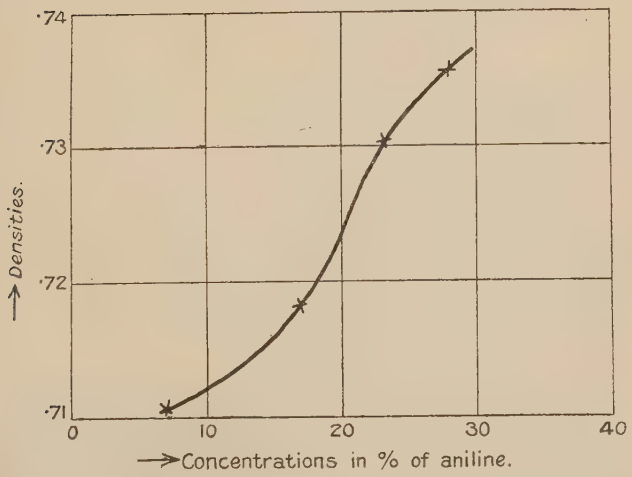
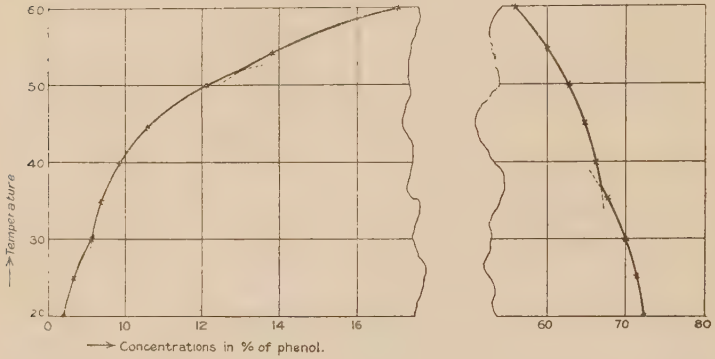


Fig. 7 shows the relation between the densities and concentrations for saturated solutions of the same system

between 0° and 20° C. for the upper layer, *i. e.* for the branch on the right-hand side in fig. 5. The relation for the other layer is substantially of the same character.

It is obvious that the asymmetric parabola with densities plotted as abscissæ, being very nearly smooth, must become strongly discontinuous if concentrations are plotted instead of densities. See fig. 8, which represents the data for the system phenol-water, taken from the Landolt Börnstein Tables, where there are many similar examples of the same kind.

Fig. 8.



It is noteworthy that by plotting the excess of concentration of one layer compared with the other, a strongly discontinuous curve is obtained which is represented in fig. 9.

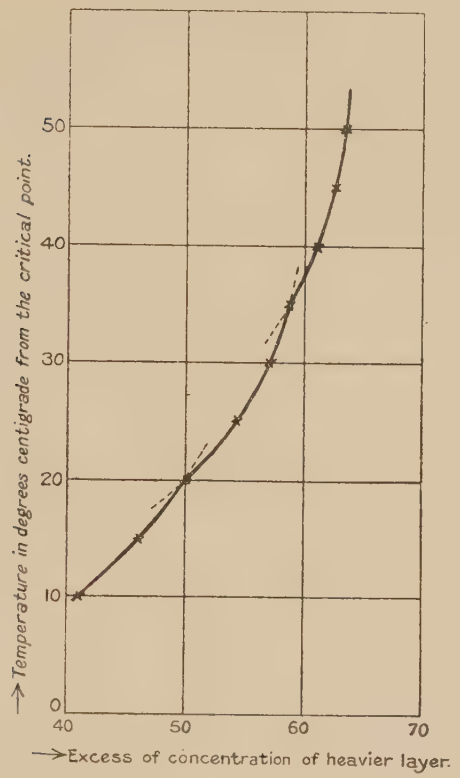
It is similar in character to the δ-temperature curves dealt with in my previous paper (where δ is the difference between the density of liquid and its vapour), but its discontinuity is much more pronounced.

By plotting d (the difference of densities of two saturated liquid layers) against temperatures, I obtained a curve of the same character as the δ-curve. It also follows the horizontal axis very closely, starting from the critical point, and its equation must be also of the form

$$Ae^{\lambda d} = T + A.$$

It thus appears that the discontinuity is an intrinsic property of liquid systems. By plotting densities against temperatures the discontinuity is partially compensated, but it is still there.

Fig. 9.



§ 2. *Interfacial Tension.*

It is also interesting to follow up the similarity between the systems liquid-vapour and liquid-liquid from the point of view of surface-tension.

By comparing the two classes of phenomena, one cannot help noticing the following :—

When a system liquid-liquid is cooled just below the critical point at which a homogeneous solution separates into two liquid layers, *the meniscus between the two layers is flat.* I have photographed the same in the vicinity of the critical point with considerable magnification, and I found that even at a certain distance from the critical point it remains very nearly flat. The measurement of interfacial tension in these regions often presents great difficulties, and for this reason I determined the surface-tensions of both coexisting layers separately. I found that even at a certain

distance from the critical point both the layers have practically equal surface-tension, or at least no appreciable difference can be detected by the capillary method. This is a sequel of a general law for the whole critical region all round the critical point, that the surface-tension is independent of concentration in this region. In other words, the interfacial tension α_{12} is very nearly $=0$, and the curve representing the change of α_{12} with temperature from the critical point follows very closely the axis of temperatures, and its equation must be of the form

$$\alpha_{12}+A=Ae^{\lambda T}.$$

Now, in systems liquid-vapour, when the critical point is reached and the meniscus appears in the middle of the tube, one cannot help noticing that the meniscus is flat. The rise of the liquid in a capillary tube becomes appreciable only at a certain distance from the critical point. At the critical point, or in the immediate vicinity of it, the capillary rise is not detectable experimentally, and some authors even observed a slight capillary depression and not rise, although this was afterwards attributed to the experimental errors *.

Anyway the surface-tension α is very small at the start from the critical point, it follows very closely the temperature axis, and, as shown in my previous paper, its equation is

$$\alpha+A=Ae^{\lambda T}.$$

The fact that the meniscus at the critical point is flat is very significant. *It means that the gaseous phase has surface-tension equal to that of the liquid phase.* We have no method of measuring the surface-tension of the vapour, nor of that of a liquid. What we really do is to measure the tension at the interface between liquid and vapour which is equal to the difference of surface-tensions of the two coexisting phases.

In this sense what we call surface-tension α in systems liquid-vapour is an analogue of the interfacial tension in systems liquid-liquid. The fact that the interfacial tension remains negligible even at some distance below the critical point indicates that in these systems the surface-tension is also independent of concentration. It is therefore reasonable to conclude that such will also be the case above the critical point.

The same applies to the normal pressures. The normal pressure of both phases is the same at the critical point and

* Wolf, *Ann. de Ch. et Phys.* (3) xlix. p. 270 (1857); Drion, *ibid.* (3) lvi. p. 221 (1859); Clark, Phil. Mag. (5) x. p. 145 (1880).

in its immediate vicinity. At lower temperatures their difference becomes more and more appreciable.

This subject will be further discussed in the section on conditions of equilibrium.

II.

Conditions of Equilibrium.

To define conditions of equilibrium between two coexisting phases, I shall treat the systems liquid-liquid in the first place.

It is quite natural to ask oneself the question: Why do they not mix on shaking? One would expect that the greater the difference of concentration, the greater must be their tendency to mix.

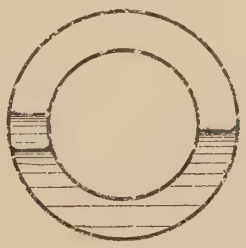
And yet the experimental evidence tells us that quite a number of physical properties in the systems of that kind remain constant with the increase of concentration. And particularly such properties as depend upon the number of molecules and not their nature.

Vapour-Pressure.

Thus, *for example, the vapour-pressures are independent of concentrations, even well outside the solubility curve* in the regions of an unlimited mutual solubility *. The depression of vapour-pressure in a solution is proportional to the number of molecules dissolved (Raoult's law).

The two liquids in equilibrium must have the same pressure and composition of vapour (Konovalov's law), because otherwise there can be no equilibrium.

Fig. 10.



Imagine an annular ring, as shown in fig. 10, containing two layers in equilibrium. If both layers did not have the same vapour-pressure there would be a continuous distillation—a kind of perpetual motion.

* See D. Konovalov, *Ann. d. Phys.* x. p. 315 (1903).

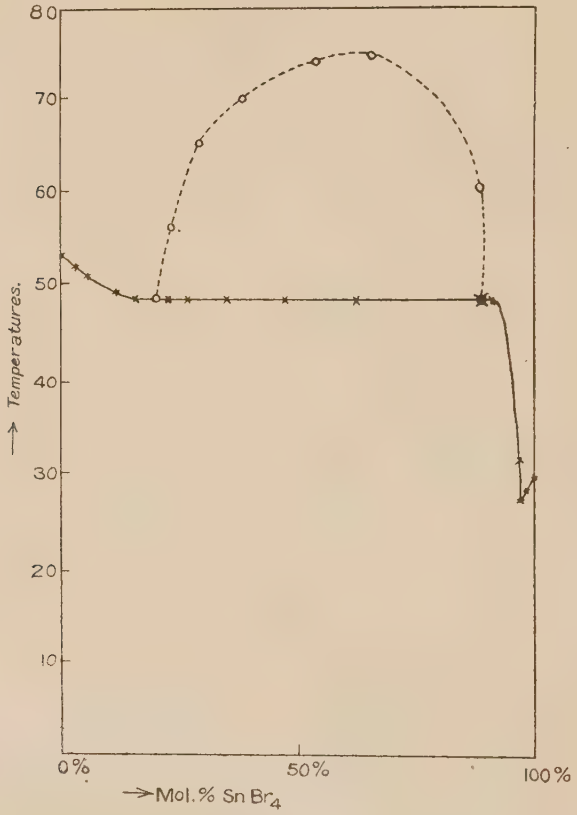
Thus the above law is in accordance with the laws of thermodynamics.

But the above considerations do not tell us how to reconcile Konovalov's law with Raoult's law.

Freezing Temperature.

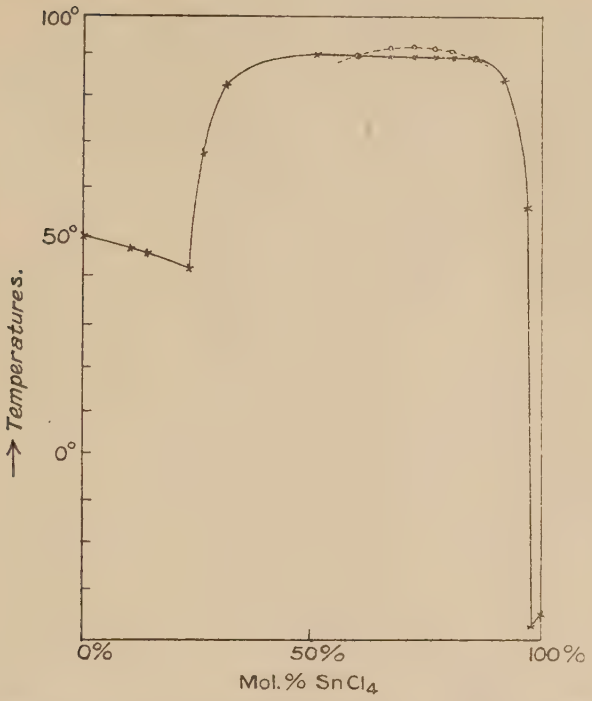
The study of freezing-point curves shows that the *freezing temperature is also independent of concentration within certain limits.*

Fig. 11.



I chose for this purpose two systems, viz. methyl oxalate and stannic bromide, and methyl oxalate and stannic chloride. The two pairs just reproduce experimentally the two possible cases, which were demonstrated by two rough diagrams in my paper (Phil. Mag. xxxvi. Nov. 1918, p. 394).

Fig. 12.



These results are represented in figs. 11 and 12, and the experimental figures given in the following tables.

TABLE I.

Methyl-Oxalate—Stannic Bromide.

Solubility data.

Mol. per cent. of $SnBr_4$.	Temperature.	Mol. per cent. of $SnBr_4$.	Temperature.
20·0	49°·2	65·4	73°·3
29·2	52°·6	90·1	61°·5
37·0	69°·8	90·5	49°·2
54·4	74°·9		

In this table temperatures are given at which solutions of a given composition begin to separate into two phases.

TABLE II.

Methyl-Oxalate—Stannic Bromide.

Mol. per cent. of $SnBr_4$.	Freezing Temperature.	Mol. per cent. of $SnBr_4$.	Freezing Temperature.
0	53·2	54·4	49·2
·97	52·7	65·4	49·2
2·4	52·3	90·1	49·2
7·1	50·7	90·5	49·2
13·0	49·7	92·0	49·2
16·2	49·2	97·0	31·0
20·0	49·2	97·8	27·8
22·8	49·2	99·1	28·4
29·2	49·2	100	29·0
37·0	49·2		

TABLE III.

Methyl-Oxalate—Stannic Chloride.

Mol. per cent. of $SnCl_4$.	Freezing Temperature.	Mol. per cent. of $SnCl_4$.	Freezing Temperature.
0	53·2	71·3	92
11·9	48·0	75·3	92
13·6	47·0	80·4	92
20·2	45	80·7	92
25·1	69	85·0	93
31·1	86	91·2	86
50·3	92	98·0	60
59·7	92	99·5	−33·2
68·1	92	100	−32·2

The solubility data could not be determined accurately because of instability of this system just in the region of

partial solubility. They are comprised between about 94 and 92° C. and are shown by a dotted curve in fig. 12.

The figures were obtained by observing the temperature at which the solid phase disappears in a solution of a definite concentration sealed in a glass tube, and subjected to energetic shaking in a bath of a suitable transparent liquid. The underlined figures were obtained by a cryoscopic method.

Both curves show that on addition of one of the components the freezing-point *curve becomes very nearly horizontal even outside the limits of solubility, and the two layers have the same freezing-point.*

The latter fact has already been mentioned in my paper of 1918 (*loc. cit.*). There I expressed the view that both solutions must be regarded as solutions in the same solvent, as they are situated on one side of the eutectic point as in fig. 11, or between two eutectic points as in fig. 12. In the latter case there is an evidence of a definite combination between the components of the solution, separable in crystalline form. It thus appears that we have to deal with a solvent of a somewhat complex nature. Both the saturated layers must be regarded as solutions in this solvent.

The fact that two layers in equilibrium freeze at the same temperature is likewise in agreement with the laws of thermodynamics, but it is in apparent contradiction with Raoult's law, according to which the depression of freezing-point is proportional to the number of molecules dissolved.

Boiling Temperatures.

There is a similar law concerning boiling temperatures often known as Beckmann's law, stating that the increase in the boiling temperature is proportional to the number of molecules dissolved. Like the two other properties previously discussed, the boiling temperature always remains constant and the same for both layers in equilibrium.

Interpretation of the above results.

Now I shall discuss these phenomena in the light of Raoult's law.

According to this law the lowering of freezing-point or vapour-pressure is proportional to the number of molecules dissolved in a given solvent. The lowering of freezing-point or vapour-pressure in the same solvent produced by equimolecular quantities of different substances is the same.

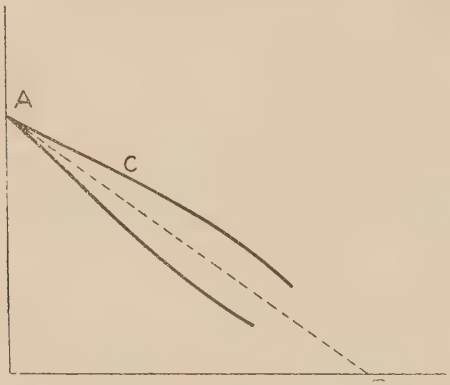
This law is said to be applicable to the very dilute solutions, in other words, those which must behave like

perfect gases. In practice this law is never strictly obeyed. Instead of proceeding along the straight line AB, fig. 13, the curve generally departs from it with the increase of concentration one way or another. That is why for determination of molecular weight of the dissolved body very dilute concentrations are generally used.

However, the liquids do not behave like gases, and according to my theory the change of *temperature is always accompanied by a certain change in the molecular state.* The results discussed in this paper suggest that in *solutions the change of concentration may cause a similar effect*—due to the interaction of the molecules. It thus appears that the very fact of change of temperature and concentration is one of the reasons why Raoult's law should not be obeyed in its pure form.

I thus find that to reconcile the laws of Raoult (and Beckmann respectively) with the above experimental facts,

Fig. 13.



it is necessary to make a special hypothesis as to the molecular state of dissolved particles in solutions.

I assume that, in all those regions where the properties mentioned do not change with concentration, the particles added combine with some particles in solution without increasing the number of particles dissolved.

Such an hypothesis does away with all difficulties in understanding these phenomena, and it is in agreement with evidence of quite a different nature, as will be shown shortly.

At this moment it is necessary to add that the above interpretation will be disputed by some people on the ground that Raoult's law and the like are only valid in the region of very low concentration.

Fig. 13 shows how the above properties change with

concentration according to Raoult's law (the straight line), and how they depart from it in practice one way or another.

These deviations may be also due to the same causes as the deviations from Boyle's law in gaseous systems. But for the object of this work it is sufficient to mention one possible case.

Take a certain point C on the diagram fig. 13 which has departed from the straight line appreciably. Suppose that at this stage the newly added molecules of the component begin to combine with some molecules in solution without increasing their number. We can then expect that the property will not change any more with the increase of concentration and the curve will become horizontal (not as is shown in fig. 13) for a certain range of concentrations.

If the number of molecules remains the same and the molecular field exercised by the new molecules is not substantially changed, we may expect that the surface-tension will be also independent of concentration, *and such is actually the case* in the critical region.

If these deviations from the simple laws were only due to such attractions as assumed by van der Waals, the surface-tension ought to increase with the increase of concentration. The increased concentration in such case means a larger number of molecules at a smaller distance, when the molecular forces become much greater.

I thus arrived at the conclusion that, in order to produce a system capable of separating into two layers, it is necessary that the number of molecules in solution remain unaltered with the increase of concentration. This condition, however, is not sufficient, because we saw instances of it in regions outside the boundaries of limited solubility. Apparently the separation into two layers does not take place until the molecular complex is present in a certain quantity.

As I said, both temperature and concentration may stimulate the formation of these complexes in several stages, such as

$$A + A = A_2$$

$$2A_2 = A_4$$

$$2A_4 = A_8$$

and so on.

It will be shown later on that, in accordance with the existing evidence, the above scheme represents molecular changes taking place in the system phenol-water.

Systems Liquid-Vapour.

Now, let us see how far the above considerations can be extended over systems liquid-vapour. In this case such properties as freezing temperature and boiling temperature are of no use to us.

However, the relation between volume, *i. e.* concentration, and pressure in the critical region liquid-vapour is very significant. It is well known that well outside the limits of a symmetric parabola (within which the two phases coexist) the pressure remains very nearly independent of volume, *i. e.*, concentration.

It thus appears that there is a tendency in these systems as well to form complex molecules above, and all round the critical point. Changes of both temperature and concentration seem to favour their formation, and apparently the separation into two phases takes place when these properties reach a certain value.

This process is discontinuous, consisting of a series of distinct stages. Speaking only very roughly, one can describe the process of liquefaction as indicating continuity between the two states.

Thus, all facts mentioned in this paper show that the essential condition of equilibrium between two phases is a definite relation between the number of molecules in the two phases.

In the following section I will show that important conclusions of the same nature can be derived from consideration of conditions at the interface, which are necessary for the maintenance of equilibrium.

III.

The Law of Difference as a Condition of Equilibrium and its Consequences.

In the preceding section certain physical properties were discussed with the view of specifying the conditions of equilibrium between two coexisting phases.

All the above data pointed to the fact that for the stable equilibrium it is necessary that the two phases should contain an equal number of molecules per unit volume.

It has been shown in my paper of 1918 that some considerations of a totally different nature lead to the same result.

Long ago I found that if the two saturated layers are in a state of equilibrium, the conditions

$$\alpha_{12} = \alpha_1 - \alpha_2$$

must be fulfilled, which I shall call for simplicity *the law of*

difference. I tried many times to prove the truth of the above equation as a condition of equilibrium from energy consideration.

If it is easy to show the truth of Konovalov's law (the equality of vapour-pressure) by means of a scheme shown in fig. 10, no considerations of that kind seemed to throw any light on the law of difference. I very soon came to the conclusion that no further step could be made in the matter unless something more definite is known about the structure of atoms and molecules, and the nature of the field of force exercised by them. This was the reason why I temporarily gave up work on these lines and began to work in what may appear at first sight a totally different domain—radioactivity. The development of this subject already then indicated that it would lead to a more intimate knowledge of the structure of matter.

When Rutherford published his theory of the atom (1911), I immediately felt that it was an impetus for the work I was interested in. I then went to Cambridge and devoted there most of my time to the development of the theory of surface-tension as a result of electrical and magnetic attractions exercised by electrical matter. This theory was ready in 1914 but its publication was delayed by the War, and it first appeared in 1918 (Phil. Mag. vol. xxxvi. Nov. 1918). In this paper I deduce the law of difference from relations connecting the normal pressure and surface-tension, on page 388.

It was shown there that this law could be deduced subject to the condition that the two phases in equilibrium contain an equal number of molecules per unit volume.

Now, we saw that there is strong evidence indicating that in systems liquid-vapour the conditions at the interface are subject to exactly the same laws—namely, the flat meniscus in the critical region means that the vapour and liquid have equal surface-tensions. This, together with the fact that the capillary rise in this region is very nearly $=0$, is an indication that the law of difference must hold true also for systems liquid-vapour, so that

$$\alpha = \alpha_l - \alpha_v,$$

where α_l is surface-tension of liquid and α_v is surface-tension of vapour.

Assuming that α_v is probably very small at lower temperatures, α is practically the value of surface-tension of a liquid at low temperatures.

It is also natural to assume that the equation

$$P = P_l - P_v,$$

where P_l is the normal pressure of the liquid and P_v is the normal pressure of the vapour, must hold true.

Following the same arguments as before, I can put

$$P_l = k\alpha_l n_l^{1/3},$$

where n_1 is the number of molecules per unit volume in the liquid

$$P_v = k\alpha_v n_v^{1/3},$$

where n_v is the number of molecules per unit volume in the vapour.

$$\therefore \quad P = k(\alpha_l n_l^{1/3} - \alpha_v n_v^{1/3}). \quad . \quad . \quad . \quad (1)$$

On the other side the relation between P and α must be of the form

$$P = k\alpha n^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The equation (2) has a definite physical meaning and is compatible with (1), if

$$n_l = n_v = n,$$

i. e., in a state of equilibrium there must be on either side of the interface separating the two phases an equal number of rows of molecules, each row containing the same number of molecules.

In other words

$$n_l = \frac{\delta_l}{Mx} = n_v = \frac{\delta_v}{My},$$

where δ_l is the density of liquid, δ_v that of vapour, M the molecular weight corresponding to a simple, non-associated molecule, and x and y association factors for liquid and vapour.

The above is a condition of equilibrium. It could not be deduced thermodynamically, because it involves a definite structural change, of which thermodynamics take no cognisance.

Thus, from the point of view of conditions of equilibrium, we arrive at a very important conclusion as to the molecular state of liquids at all temperatures.

Assuming that the vapour is monomolecular, *i. e.*, $y = 1$,

$$x = \frac{\delta_l}{\delta_v}.$$

Thus, *the association factor is the ratio of density of liquid to that of its saturated vapour*, if the vapour is monomolecular.

I shall try now to estimate x at temperatures corresponding to the kinks in the δ curve, as indicated in my paper of July 1925.

It should be pointed out that the figures are not accurate enough in order to see whether a kink always corresponds to a whole number of x. I leave out of consideration the question whether it is so or not, and shall only add that I do not attribute to it much importance. Experience has shown me more than once that the position of kinks indicated by different physical properties, owing to a common cause, varies as a rule, and does not coincide exactly with places corresponding to definite molecular proportions.

I thus estimate that from the critical point x acquires the following values near the kinks for ethyl acetate :—

2, 6, 18, 36, 144, 864, etc.

The latter figure corresponds to a temperature of about 50° C.

It is seen that, according to this theory, *the degree of association at low temperatures must be fairly high.*

Following the same arguments I deduced the scheme for phenol-water. In my paper of 1918, describing the law of difference for systems liquid-liquid I used the letter p for the number of molecules per unit volume, where p meant the total number of molecules per unit volume, including the solvent. The number of molecules dissolved (n_1 and n_2) must be also the same for both layers per unit volume. In this case it is more convenient (for reasons which will be explained in the subsequent paper) to express the same in terms of concentrations (C_1 and C_2),

$$n_1 = \frac{C_1}{M.x} = n_2 = \frac{C_2}{My}.$$

By determining the ratios $\frac{C_2}{C_1}$ corresponding to the kinks in the curve fig. 9, the scheme p (1137) is arrived at.

IV.

Conclusion.

The often observed departures from the laws of simple proportionality in vapours and liquids, such as Boyle's law, etc., have naturally resulted in many attempts to account for them.

Amongst these theories, perhaps the most prominent position is occupied by that of van der Waals. His fundamental idea is that the deviations from Boyle's law are due to the molecular field round the molecules, which causes attraction between molecules when they are brought close together owing to external pressure. The resultant of these forces causes a diminution of pressure exercised by a given volume of gas. This inward force per unit area is called normal or molecular pressure. Its presence also necessitates the existence of a force tangential to the surface. This force per unit length is surface-tension.

Although we may have no method of directly measuring the same, the surface-tension of vapours and gases may be sometimes quite appreciable.

In this sense one cannot help recognising the value of van der Waals's theory, as having explained the necessity for surface-tension and normal pressure in gases, although in its quantitative side it often fails.

On the other hand, the old theory of de Heen, which has not received general recognition, and may be practically regarded as abandoned, undoubtedly contains an element of truth. It failed chiefly owing to the want of experimental data in those days on which it could be tested.

I started my work without having any definite views of any kind.

Only after I followed up the analogy between systems liquid-liquid and liquid-gas, which, I believe, are governed by identical laws, have I formed a theory of my own.

I have come to the conclusion that the molecular field cannot account for the peculiar behaviour of isoterms in the critical regions, where, as has been mentioned before, a number of physical properties are independent of concentration. Some of them are very nearly identical for the two coexisting phases in the critical region only, and some are the same so long as the two phases coexist.

Thus I found experimentally that in the systems liquid-liquid the surface-tension does not vary with concentration above the critical point in the region of complete mixability.

According to my theory it means that in the expression for surface-tension α (see Phil. Mag. xxxvi, p. 382, 1918).

$$\alpha = k\, l^2\, p^{5/3},$$

where l is the length of the doublet, and $p = \frac{\delta}{M}$ is the number of molecules per unit vol., p remains constant with the change of concentration, *i. e.*, the molecules added combine with molecules in solution, so that their number remains

the same. And it also means that the molecules formed have the same l.

This is very nearly true for two phases in equilibrium in the critical region. At lower temperatures the surface-tensions of two phases begin to differ appreciably, and yet their other properties remain the same, viz., those which indicate that the number of molecules per unit vol. is still the same in both. Therefore, in this case, the newly-formed molecules in one phase have a bigger l than in the other, and yet one can see no effect of it on other properties.

I therefore conclude that Raoult's law has nothing to do with the magnitude of the molecular field, and that the deviations from it are due to some other causes.

Thus, although I believe in the surface-tension and normal pressure of gases, I do not believe the peculiar character of isoterms in the critical regions is due to this.

I should like to illustrate the above by the following model. Imagine a rubber ball with a fairly thick wall filled with air, whose pressure can be reduced by some means, or the pressure outside it increased, which practically amounts to the same.

There will be a certain tension and normal pressure in the membrane to counterbalance the excess of external pressure. Such a system, however, is not stable, and can exist only in more or less ideal conditions. A slight disturbance will do away with the stress in the membrane, or at least part of it, and a more stable equilibrium will establish itself with diminution of volume. If, however, the ball is filled with a liquid, the external pressure will cause stress in the rubber ball, and it will increase with the external pressure.

Similarly, in systems we are interested in, the increase of concentration probably could be followed by the increase in normal pressure, if the molecules were all alike and travelled with the same velocities. But as their velocities vary within certain limits, and the field is not uniform, it is quite probable that the molecules with velocities below the average will combine as a result of increased concentration, and thereby render the system more stable.

In such a case the normal pressure will not necessarily increase with concentration, but may remain substantially the same if the doublet of combined molecules does not differ much from that of a single molecule.

In regions of high concentrations (which may be compared with the rubber ball filled with a fluid with small compressi-

bility), where the particles are close together, the molecular field will make itself felt with the increase of concentration.

I thus share the view of van der Waals so far, that I believe in a molecular field and its effect on certain properties of a system, but I do not believe the properties of critical regions are due to it.

All these phenomena can only be explained by the theory of molecular interaction.

In each of my previous papers I deal with phenomena of a widely different nature, and yet they all point to one and the same thing—the formation of complex molecules. Thus the changes of state must be invariably accompanied by the change in molecular complexity, and the formation of complex molecules begins above the critical point.

My theory also leads to the conclusion that all liquids must be highly associated at low temperatures.

It thus appears that according to the formula

$$P = k \alpha p^{1/3}$$ (Phil. Mag. xxxvi. p. 312, 1918)

connecting normal pressure, surface-tension, and the number of molecules per unit volume, one must expect a much lower value for the normal pressure of liquids at low temperatures than usually expected.

It would also mean that, if these phenomena of association remain in force in the solid state, one would expect much lower figures for the breaking stress than expected from electrical theory (which does not take into account the association and deals with single molecules), which is actually the case.

Summary.

(1) It is shown in this paper that the systems liquid-liquid (*i. e.*, those which separate into two liquid layers) and systems liquid-gas are governed by identical laws.

(2) Thus it is shown that the temperature changes in systems liquid-liquid also take place in a discontinuous manner ; the discontinuous character appears very strongly if concentrations of two saturated layers are plotted against temperatures instead of densities. It appears that both temperature and concentration changes favour the formation of complex molecules.

(3) The properties depending upon the number of molecules and not their nature, indicate that the number of molecules per unit volume remains the same with the increase of concentration in the critical regions and sometimes

outside them. The formation of complexes is a necessary condition for separation into two phases.

(4) The analogy between the two systems was extended to the conditions at the interface separating two phases. It was thus assumed that the law of difference must hold true for systems liquid-gas, with its natural consequence

$$n_l = n_v,$$

i. e., the number of molecules per unit volume in liquid is equal to the number of molecules in vapour. Or

$$\frac{\delta_l}{\mathrm{M}x} = \frac{\delta_v}{\mathrm{M}y}$$

where δ_l and δ_v are densities of liquid and vapour, M the molecular weight, and x the association factor of liquid, and y that of vapour.

(5) It is thus possible to calculate the association factor at all temperatures and to see that its value becomes fairly high at lower temperatures.

(6) In both systems one can recognize definite molecular changes. The difference between systems liquid-liquid and liquid-gas is that in the latter case these changes take place between molecules in a space not otherwise filled, whereas in the former they take place within a liquid acting as dissolvent.

The subject will be treated more fully in the subsequent paper.

CIII. *Dimensional Analysis.*

By Norman Campbell, *Sc.D.**

Summary.

A consideration of Mrs. Ehrenfest-Afanassjewa's principle of similitude. Her conclusion that results can be based only on a full knowledge of the laws determining the behaviour of the system is welcomed; but it is argued that her representation of the argument as primarily mathematical is misleading. The mathematical arguments involved are so simple as not to be worth stating; all the difficulties are physical. Any suggestion that results can be obtained by juggling with symbols and neglecting entirely the physical relations involved can only give fresh life to the fallacies of "dimensional analysis."

Mrs. Ehrenfest-Afanassjewa says that the object of her paper is to promote agreement among writers on this

* Communicated by the Author.

subject *. Since she names me specifically, perhaps I may explain how far she has attained her object.

I agree with her completely, against the "dimensional analysts," as to the conditions in which the argument from dimensions is applicable. The systems must be similar and the laws governing their behaviour must be completely known. Since both of us, starting from opposite points of view with very different predispositions, reach this conclusion, perhaps it will be accepted generally and the air of mystery which surrounds the argument removed by the deletion of all implications to the contrary from our text-books.

On the other hand, she apparently agrees with the dimensional analysts in thinking that the argument can be expressed mathematically: here I differ completely. The only distinctively mathematical proposition that it employs (namely, that multiplication is distributive and associative) is so elementary that it is assumed and not proved in her analysis. The introduction of elaborate symbolism is not merely superfluous, but positively misleading. It concentrates attention on "elegant irrelevancies" and distracts it from essentials. It suggests that the circumstances in which the argument is applicable are far wider than they actually are, and thus prepares the way for all the charlatanry with which the word *dimensions* has unfortunately become associated.

This contention cannot be established except by stating the argument once more †. It will tend to brevity if only the simplest example is considered. The experimental fact stated in the numerical law

$$s = \tfrac{1}{2} f t^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is that if, in certain conditions, we measure s, the length that a particle has traversed from rest, and t, the period occupied in the traverse, then s is proportional to t^2. In any particular experiment the numerical value of f depends entirely on the units adopted for measuring s and t, the mode of dependence being indicated by the conventional assignment of dimensions; the dimensions thus assigned express the mathematical form of the numerical law. But we find that there are different experimental conditions, in all of which a length s traversed from rest is proportional to the square of t, the period occupied in the traverse, and yet

* T. Ehrenfest-Afanassjewa, Phil. Mag. i. p. 257 (1926).

† What follows is merely a summary of the full argument and analysis contained in Chapts. XIV. and XV. of my 'Physics.'

the factor of proportionality is different, although the same units are employed. Different systems involving a particle moving according to a law of the same form are characterized by different numerical values of f; f is a magnitude capable of different values. In this it resembles s and t; but it differs from them because, while s and t can be measured without any reference to numerical law, the measurement of f depends wholly on the truth of the law (1). Any physically significant statement about f implies that truth of (1); to say that a statement is characterized by an acceleration is precisely the same thing as to say that it is characterized by some particle moving according to (1).

We are now presented with a number of systems of which we are informed that each is characterized by a period T, a length S, and an acceleration F, each of these quantities being completely determined by the other two. We ask whether, and if so why, it is legitimate to conclude that, if the suffixes refer to different systems,

$$\frac{S_m}{S_n} = \frac{F_m T_m^2}{F_n T_n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The answer depends entirely upon the physical relations between S, T, F—that is to say, upon the kind of experiment we are making when we determine them. Every numerical law states both a mathematical relation and a physical relation; two laws in which the mathematical relation is the same may differ in their physical relations and *vice versa*. Thus the mathematical relations between the coordinates of a rectangular hyperbola referred to its asymptotes is the same as the mathematical relation between the pressure and volume of a perfect gas at constant temperature; but the physical relation is utterly different. Or, again, the physical relation of the coordinates of a hyperbola referred to its asymptotes is the same as the physical relation of the coordinates referred to any other axes, but the mathematical relation is different. Now it may happen that the physical relation between S, T, F is the same as that between s, t, f in (1)—that is to say, T may again be the period occupied by some particle in traversing a length S. In that case, and in that case only, (2) can be deduced by pure mathematical reasoning. For the statement that F is characteristic of the motion can only mean that in each system

$$S = \tfrac{1}{2} F T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3);$$

if it does not mean that, the statement is not merely false,

but meaningless. (2) is a direct mathematical consequence of (3); it does not involve any additional assumption—such as that the systems are similar.

But when the question is raised, the physical relations of S, T, F are never actually those of (1); for example, the period of a pendulum is not the period occupied by a particle in falling down its length. When a difference of physical relationship is introduced, mathematics alone cannot possibly answer the question; for physical relations lie wholly outside the province of mathematics. In order to deduce from (1) anything about S. T, F, some assumption must be introduced concerning the physical connexion between these quantities and the s, t, f to which (1) refers. Such an assumption is the proposition that the systems are completely similar physically—that is to say that, if x_m is a magnitude of any kind characteristic of one system, then there is a magnitude of the same kind x_n characteristic of the other, and the ratio x_m/x_n is the same for all magnitudes of this kind. From this proposition the desired conclusion follows at once. For since the systems are characterised by accelerations, each of them must be characterised by a length and a period such that

$$s_m = \tfrac{1}{2} f_m t_m^2 \quad \text{and} \quad s_n = \tfrac{1}{2} f_n t_n^2. \quad . \quad . \quad . \quad (4)$$

But $$\frac{S_m}{S_n} = \frac{s_m}{s_n}; \quad \frac{T_m}{T_n} = \frac{t_m}{t_n}; \quad \frac{F_m}{F_n} = \frac{f_m}{f_n}, \quad . \quad . \quad . \quad (5)$$

and (2) follows.

Here, again, the mathematical argument is so simple that it is hardly worth writing down; it certainly does not justify the introduction of the elaborate conception of invariance under transformation. The whole difficulty lies in the physical assumption of similarity. How are we to know that the systems are physically similar, unless we have such a complete knowledge of them that we are already aware of the proposition we profess to prove? The answer is, of course, that we never do know; we merely have reasons to suspect. The reasons may be of many different kinds; they may be good or bad; but they are always purely physical reasons, based, rightly or wrongly, on observations of the systems and not on jugglings with symbols. Thus, in the case of the pendulum, our reason is that the period of the pendulum seems to be the physical sum of elementary periods, during each of which it may be supposed to move with constant acceleration; that is a reason which can appeal only to those who have seen a

pendulum swing. In other cases, the reason may be much more complicated and far less immediately obvious ; but it is always a reason of the same kind.

If the logic of physical relations were developed as well as that of mathematical relations, it might be possible to reduce these reasons to some simple general principle. But it is not, and perhaps never will be. And while it is not, every application of the argument must be considered and judged individually. The matter is really even more difficult than has been suggested ; for very few, if any, systems are *completely* similar, and *complete* similarity is not actually required ; we have not to judge between the absence or presence of a definite quality, but of a degree of that quality sufficient for the immediate purpose. The only rule that can be given is, I think, that given in my previous paper *. If we can write down a differential equation of the system, and if we know (this is a very large assumption) that the solution of it will lead to some relation involving the magnitudes between which we are seeking a law, then it is permissible to conclude that there is similarity between these magnitudes and those of the same kind involved in the differential equation.

These considerations are so simple and the conclusion, that it is impossible to express the argument in mathematical terms alone, is so obvious that some explanation seems to be needed why they have ever been overlooked. The cause is probably two-fold. First, it is thought that, if the argument attains without apparent mathematical argument results attainable otherwise only by the aid of complicated analysis, it must contain all that analysis somewhere in an exceedingly condensed form. But it does not attain the results of mathematical analysis ; it never proves anything in the mathematical sense, and it never leads to numerical values. Second, it is thought that what is common to all forms of the argument must be what is important in all forms. This is simply untrue. The important part of the argument, the proposition which leads to the valuable result or (if it is false) to error is different in different applications. If all the time and labour that have been devoted to elaborating irrelevant generalities had been devoted to a careful analysis of individual instances, it would have been a great deal better spent.

Finally, a few remarks may be offered on the examples of numerical laws from which Mrs. Ehrenfest-Afanassjewa

* Phil. Mag. xlvii. p. 481 (1924).

starts her argument; for, although I am not quite sure what conclusion she draws from them, they illustrate well some complexities.

Law (ii.) involves a universal constant. The assignment of dimensions to such a constant expresses as usual the mathematical form of a numerical law. Accordingly, if we include the universal constant among the quantities characteristic of the system, we can make any deductions that could have been made if it had been a derived magnitude. But if we select the magnitudes characteristic of the system by noting how its behaviour changes when certain alterations are made, we shall be led to omit the universal constant and arrive at erroneous conclusions. The experimental fact that the period of geometrically similar pendulums changes only with changes in their length and gravitational acceleration does not establish (2); for there may be some law involving a numerical constant which has the same value for all pendulums whatever their length and whatever the gravitational acceleration. The neglect of this consideration is one of the most fruitful sources of error, which is deliberately encouraged by "dimensional analysis," but would certainly be avoided by Mrs. Ehrenfest-Afanassjewa's scheme.

In law (iii.),

$$f = ks/r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where f is an angle, s the arc and r the radius, the dimensions of k give no indication of the form of the law and no conclusions can be drawn from them. But this apparent exception illustrates well the necessity for considering physical as well as mathematical relations. s and r are physically different; the experimenter has no difficulty in deciding whether he is measuring an arc or a radius. The experimental fact that f is proportional to the ratio s/r would emerge equally well if s and r were measured in different units; but it would not emerge if s or r were measured sometimes in one unit and sometimes in another. In fact, the same measuring instrument would not actually be used for s and r; different instruments would be used and one calibrated in terms of the other. This calibration is a mere convenience in comparing our results with those of others. If we are to get the most out of the essentially physical argument from dimensions, we must neither include anything unessential to experiment nor exclude anything essential. Physically distinct magnitudes must be distinguished, and

the possibility of measuring them in different units recognised. If this is done, k has the dimensions (angle) . (radius) . $(\text{arc})^{-1}$, and the dimensions represent as usual the form of the law.

It may be pointed out that this example is exactly analogous to that of the Child-Langmuir equation discussed in my previous paper. There the failure of the argument arose from the confusion of the physically distinct lengths parallel and perpendicular to the field.

March 6th, 1926.

CIV. *Results of Crystal Analysis.* *By* L. Vegard, *Professor of Physics at the University of Oslo* *.

§ 1. In previous papers † published in 1916 I gave the structure of the isomorphic minerals zircon ($ZrSiO_4$), rutile (TiO_2), and cassiterite (SnO_2), and of the mineral anatase (TiO_2). These structures were found by means of the ionization method of Bragg. Spectra of various orders for the K_α line from Rh were obtained from the principal point-planes such as (100) (001) (110) (111).

At the same time I commenced with the same method the analysis of another interesting tetragonal group of which cheelite ($CaWO_4$) and powellite ($CaMoO_4$) are typical members. This analysis was not completed, and the results obtained were therefore not published.

Some years ago, when I had set up an arrangement for analysis by means of the powder method of Debye and Scherrer, I determined to apply this method to the analysis of these groups of minerals, partly to verify the results previously obtained by means of the spectrometer method and partly to complete the analysis of the cheelite group. This work was already completed two years ago, but as my time has been greatly absorbed by other investigations, the publication of the results was delayed.

The experimental arrangement has already been described in previous papers.

The reflexion angle (ϕ) of each line on the spectrogram

* Communicated by the Author.

† L. Vegard: "Results of Crystal Analysis," Phil. Mag. xxxii. p. 65 (1916)—Paper I. *Ibid.*, III., Phil. Mag. xxxii. p. 505 (1916)—Paper II.

was found from the relation

$$\phi = \frac{l - \epsilon}{2r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $2l$ is the distance between two corresponding lines on the film (symmetrically situated with regard to the centre), r is radius of camera, ϵ is a correction term characteristic of the camera and the substance, but which was found to be approximately independent of ϕ.

The lines observed on the spectrogram are then to be identified or referred to corresponding point-planes of reflexion by means of the formula :

$$\left(\frac{2a}{\lambda}\sin\phi\right)^2 = \left(h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2\right). \quad . \quad . \quad (2)$$

a is the side of the basis, c the height of the elementary lattice, h_1, h_2, h_3 the Millerian indices of the reflecting planes. A copper anticathode was used, and for the K-radiation we have

$$\lambda_\alpha = 1{\cdot}54\ \text{A},$$
$$\lambda_\beta = 1{\cdot}39\ \text{Å}.$$

In the present case values of a and c were known from the previous observations by means of the ionization spectrometer.

The identification of the lines, therefore, merely required a direct calculation of both sides of the equation (2).

In order to obtain the best possible agreement between observed and calculated values throughout the whole spectrum, the dimensions of the elementary lattice (a and c) had to be chosen slightly different from those found by the spectrometer method.

The main interest of this paper is attached to the exact determinations of the parameters of the lattices, which are based on considerations regarding the relative intensities of the lines. The observed relative intensities were directly estimated. This gives no accurate values, but we get the typical distribution of intensities, and that is sufficient for our present purpose.

The theoretical value of the intensities will be put proportional to the expression

$$\mathrm{I} = \nu\left(\frac{\mathrm{S}}{\sin\phi}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where S is the structure factor, ν the relative frequency of the reflecting planes.

I. Anatase (TiO_2).

§ 2. This crystal belongs to the ditetragonal, bipyramidal class, and the axis ratio $\frac{c}{a} = 1{\cdot}777$.

My original analysis * gave for the elementary lattice:

$$a = 5{\cdot}27 \text{ Å},$$
$$c = 9{\cdot}37 \text{ Å}.$$

The elementary lattice contains 8 molecules TiO_2.

The Ti-atoms were found to form a pseudocubic lattice of the diamond type.

The O-atoms were arranged in two lattices of the same type and placed in such a way that they can be brought to coincidence with the Ti-lattice through motions along a distance $+l$ and $-l$ respectively.

Thus the lattice has merely one parameter l, or we may more conveniently introduce an angular parameter

$$\gamma = 2\pi \frac{l}{c}.$$

By means of the spectrometer method I found

$$\frac{l}{c} = 5/24, \quad \text{or} \quad \gamma = 75°.$$

Selecting a symmetry centre of the lattice as origin of the coordinates, we easily deduce the following simple equation for the structure factor S:

$$S = \cos A \,(\mathrm{Ti} + 2\mathrm{O}\cos h_3\gamma), \quad . \quad . \quad . \quad . \quad (4)$$

where

$$A = \frac{\pi}{4}(h_1 + h_2 + h_3).$$

We have to consider the following three cases:

(*a*) $h_1 + h_2 + h_3 = 4n$, then $\cos A = \pm 1$ and
$S = \mathrm{Ti} + 2\mathrm{O}\cos h_3\gamma$.

(*b*) $h_1 + h_2 + h_3 = 4n \pm 1$, then $\cos A = \pm \frac{1}{\sqrt{2}}$ and
$S = \frac{1}{\sqrt{2}}(\mathrm{Ti} + 2\mathrm{O}\cos h_3\gamma)$.

(*c*) $h_1 + h_2 + h_3 = 4n + 2$, then $\cos A = 0$ and
$S = 0$.

* Paper II.

Thus the lattice gives no reflexion for planes whose indices fulfil the condition $\Sigma h = 2(2n+1)$, where n is a whole number.

The indices corresponding to the lines observed from anatase are given in Table I., and we see, in accordance with theory, that none of the observed lines fulfil the conditions (*c*).

From the intensities of the lines corresponding to case (*a*) we were able to conclude that the angle γ could not differ much from 90°, but for this group of lines we get the same intensity for $90° + \epsilon$ and $90° - \epsilon$.

When, however, we take into account the second group (*b*) of lines, we find that γ must be smaller than 90°.

Then the intensities of the lines were calculated for a number of values of γ between 70° and 80°. The best correspondence between calculated and observed values was found for $\gamma = 75°$, which is the very same value as that originally found, and thus the powder method gives exactly the same lattice as the Bragg reflexion method.

The results of our calculations both as regards position and intensities of the lines of the powder spectrum from anatase are given in Table I., and a graphical representation is given in fig. 1.

The space group of the lattice is D_{4h}^{19} after Niggli, which gives a symmetry of the crystal corresponding to the ditetragonal-bipyramidal class.

A model of the structure is given in my previous publication.

The positions of the atoms in a (110) plane are shown in fig. 2 A, and for a (100) plane are given in fig. 2 B.

The atoms belonging to the two face-centred lattices are marked I and II respectively.

From fig. 2 A we see that each O-atom is surrounded by three Ti-atoms. For the centre distances we get :

$$O_I - Ti = 1{\cdot}99 \text{ Å}$$

and $$O_2 - Ti = \sqrt{\left(\frac{a}{4}\right)^2 - \left(\frac{1}{4} - l\right)^2 c^2} = 1{\cdot}94 \text{ Å}.$$

With the particular value of the parameter l derived from the X-ray analysis, we thus find that the two centre distances are very nearly equal. This means that we may regard the crystal as formed by packed spherical atoms.

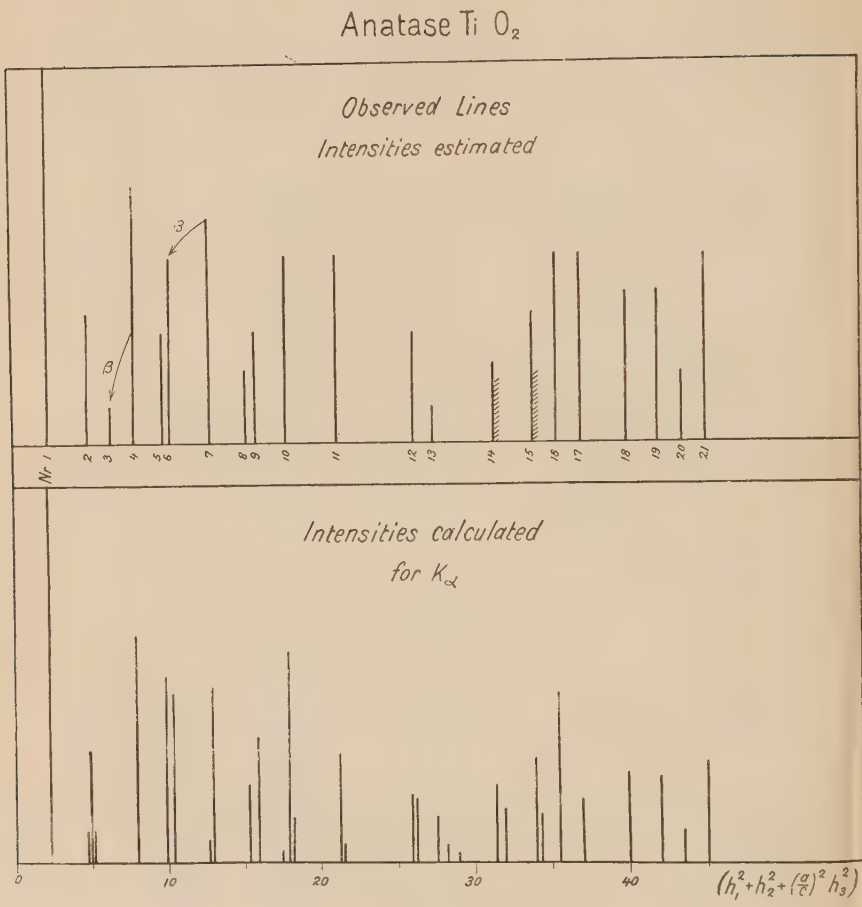
TABLE I.

Anatase, TiO_2.

$a = 5{\cdot}37$ Å. $c = 9{\cdot}54$ Å. $c/a = 1{\cdot}777$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
1	12·44	2·29	2·32	1.1.1	100	100
			4·84	1.1.3	9	
2	18·71	5·04	5·06	0.0.4	30	35
			5·26	2.0.2	9	
3	21·27	(7·88)β	(8·00)	(2.2.0)		
4	23·77	7·97	8·00	2.2.0	61	70
5	26·65	9·90	9·90	1·1.5	48	30
6	27·27	10·32	10·32	3.1.1	45	50
			12·84	3.1.3	6	
7	30·93	12·98	13·06	2.2.4	47	60
8	33·86	15·26	15·37	2.0.6	21	20
9	34·75	15·97	16·00	4.0.0	31	30
			17·48	1.1.7	3	
10	37·15	17·92	17·90	3.1.5	54	50
			18·32	3.3.1	12	
			20·22	0.0.8	2	
			20·84	3.3.3	2	
11	41·02	21·16	21·06	4.0.4	29	50
			21·26	4.2.2	4	
			25·48	3.1.7	1	
			25·90	3.3.5	18	
12	46·87	26·13	26·32	5.1.1	17	30
13	48·64	27·41	27·60	1.1.9	13	10
			28·22	2.2.8	5	
			28·84	5.1.3	3	
14	53·24	31·55	31·37	4.2.6	21	20
			32·00	4.4.0	15	
			33·48	3.3.7	1	
			33·90	5.1.5	28	
15	56·64	34·28				35
			34·32	5.3.1	13	
			35·60	2.0.10	24	
16	58·68	35·87				50
			35·60	3.1.9	21	
			36·84	5.3.3	2	
			37·06	6.0.2	1	
17	60·77	37·42				50
			37·16	4.4.4	17	
18	64·84	40·27	40·00	6.2.0	24	40
			40·24	1.1.11	3	
			40·48	5.1.7	1	
19	67·87	42·18	41·90	5.3.5	23	40
20	71·16	43·60	43·60	3.3.9	9	20
21	74·30	45·11	45·06	6.2.4	27	50

Fig. 1.



If we put $\gamma = 73°{\cdot}5$ instead of 75° the two centre distances would be the same and equal to 1·95 Å, or indicating by ρ the atomic radius,

$$\rho_O + \rho_{Ti} = 1{\cdot}95.$$

If now we assume oxygen to be present as a negative ion O− −, it should according to W. L. Bragg* have a fairly large radius of about 1·35 Å.

* W. L. Bragg, Comm. from Roy. Inst. May 1, 1925.

The question then arises whether the structure can allow for such large dimensions of the oxygen atoms.

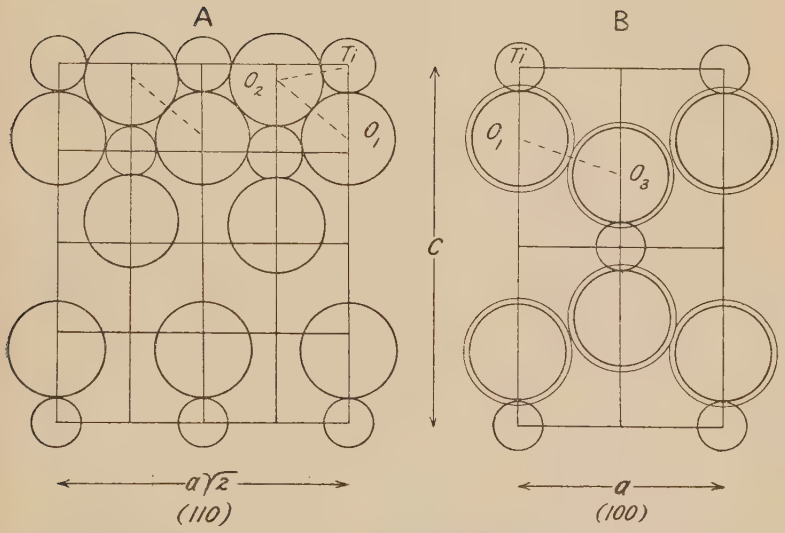
For the centre distances between two oxygen atoms we get

$$O_1-O_2 = 2{\cdot}48 \text{ Å (fig. 2 A)},$$

$$O_1-O_3 = \underset{\text{Mean}}{\frac{2{\cdot}79 \text{ Å}}{2{\cdot}64 \text{ Å}}} \text{ (fig. 2 B)}.$$

Fig. 2.

Anatase



With the radius given by Bragg the centre distance in the case of contact would be 2·70, which is near to the mean value of the two centre distances found.

If the oxygen atoms are supposed to be a little deformed so as to be not perfectly spherical, we may assume that also the oxygen atoms are mutually in contact.

This means of course that this particular type of lattice gives a high degree of stability for the atoms Ti and O with their atomic dimensions. It is clear that with other diameters of the two atoms this lattice would no longer give the same stability. Perhaps this may explain why this type of lattice is not stable in the case of SnO_2.

Assuming the diameter of oxygen in TiO_2 to be 2·64 Å, we get the radius of Ti :

$$\underline{\rho_{Ti} = 0{\cdot}63 \text{ Å}.}$$

II. The Zircon Group.

§ 3. In the paper published in 1916 the following structure was found for zircon:—

The elementary lattice ($a=9{\cdot}20$ Å, $c=5{\cdot}87$ A) contained

Table II.—Zircon.

$a = 9{\cdot}41$ Å. $c = 6{\cdot}01$ Å. $c/a = 0{\cdot}639$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I_0.	I_I.	I_{II}.
			4·45	1.1.1		25	35
1	13·59	8·25	8·00	2.2.0	70	93	86
			12·45	3.1.1		26	4
2	17·77	13·95	13·80	2.0.2	50	68	58
3	19·23	16·21	16·00	4.0.0	10	12	10
4	20·33	18·03	17·80	2.2.2	5	19	7
5	21·79	20·58	20·45	3.3.1	30	13	28
6	23·67	24·06	24·05	1.1.3	30	5	21
7	24·77	$(31{\cdot}99)_\beta$	(32·00)	(4.4.0)			
8	26·02	28·74	28·45	5.1.1	20	23	20
9	26·60	29·94	29·80	4.2.2	100	100	100
			32·00	4.4.0			
10	27·69	32·24			40	41	33
			32·05	3.1.3			
11	29·73	36·71	36·45	5.3.1	10	2	4
			39·20	0.0.4		21	9
			40·00	6.2.0			
12	31·25	40·18			35	40	28
			40·05	3.3.3			
			41·80	4.4.2		2	0
13	33·65	45·85	45·80	6.0.2	60	47	51
14	34·12	47·14	47·20	2.2.4	30	32	25
			48·05	5.1.3		14	0
			49·80	6.2.2		5	1
15	35·43	$(61{\cdot}72)_\beta$	(61·80)	(6.4.2)			
			52·45	5.5.1			
16	36·67	52·26			15	10	17
			52·45	7.1.1			
17	37·46	55·23	55·20	4.0.4	20	7	21
			56·05	5.3.3		1	6
18	38·77	$(72{\cdot}01)_\beta$	(72·00)	(6.6.0)			
			59·20	4.2.4		2	5
			60·45	7.3.1		5	0
19	40·02	61·67	61·80	6.4.2	25	30	19
			63·25	1.1.5		2	0
20	40·86	63·92	64·00	8.0.0	10	13	10
			71·20	4.4.4			
21	43·68	71·22			30	35	24
			71·25	3.1.5			
			72·00	6.6.0			
22	44·05	72·20	72·05	5.5.3	40	22	29
			72·05	7.1.3			
			76·45	7.5.1		11	3
23	46·14	77·63	77·80	8.2.2	50	28	29

TABLE II. (*continued*).—Zircon.

$a = 9{\cdot}41$ Å. $c = 6{\cdot}01$ Å. $c/a = 0{\cdot}639$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	$I_{0'}$	$I_{I.}$	$I_{II.}$
24	46·61	78·85	79·20	6.2.4	50	27	29
			78·25	3.3.5			
25	47·13	80·25	80·00	8.4.0	40	14	15
			80·05	7.3.3			
			84·45	9.1.1		1	0
			87·25	5.1.5		7	12
			89·80	8.4.2		0	2
			91·20	6.4.4		0	1
26	51·73	92·04	92·20	2.0.6	30	22	26
			92·45	9.3.1			
			95·25	5.3.5		1	2
27	53·19	95·71	96·05	7.5.3	10	13	10
			96·25	2.2.6			
			100·45	7.7.1		1	0
28	65·22	103·14	103·20	8.0.4	20	16	11
29	56·69	104·28	104·00	10.2.0	30	15	21
			104·05	9.1.3			
			107·20	8.2.4		1	4
30	58·26	107·99	108·20	4 2.6	25	33	20
			108·45	9.5.1			
31	59·15	110·06	109·80	10.0.2	50	26	28
			109·80	8.6.2			
32	59·46	110·75	111·20	6.6.4	20	24	17
			111·25	5.5.5			
			111·25	7.1.5			
			112·05	9.3.3		10	0
			113·80	10.2.2		1	1
33	63·33	119·25	119·20	8.4.4	50	16	22
			119·25	7.3.5			
			120·05	7.7.3		2	0
			120·20	4.4.6			
			122·05	1.1.7		1	0
			124·20	6.0.6		24	9
			124·45	11.1.1			
34	66·83	126·20	125·80	10.4.2	60	24	28

8 molecules $ZrSiO_4$. The Zr- as well as the Si-atoms were arranged in pseudocubic lattices of the diamond type displaced relative to each other a distance $c/2$ along the tetragonal axis.

The 32 oxygen atoms inside each elementary lattice were divided in two equal groups, one of which was considered to be closely attached to the Zr- and the second to the Si-atoms.

The oxygen atoms were not arranged in pseudocubic lattices of the diamond type, but in face-centred lattices.

The lines obtained by means of the powder method are given in Table II.

The first column gives the No. of the lines in the order of increasing reflexion angle ϕ. The second column contains the values of ϕ.

It appeared that the structure already found gave the right interpretation of all the lines observed.

The third column gives for each line the values of

$$\left(\frac{2a \sin \phi}{\lambda}\right)^2,$$

and the fourth one the corresponding values of

$$h_1^2 + h_2^2 + \left(\frac{a}{c}\right)^2 h_3^2,$$

from which we find the Millerian indices of the reflecting planes (see equation 2). These indices are given in the fifth column.

The column headed I_0 contains relative intensities of the lines as they are estimated from the film.

A few faint lines on the spectrogram are due to a reflexion of K_β, and these lines are in the table indicated by β.

As already mentioned, the structure found may be regarded as composed of face-centred lattices, and, taking a point midway between two neighbouring Zr-atoms as the origin of our coordinate system, the basis group of face-centred lattices is given by the following coordinates :—

The Zr-atoms :

$$\left[\left[\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}\right]\right] \text{ and } \left[\left[-\tfrac{1}{8}, -\tfrac{1}{8}, -\tfrac{1}{8}\right]\right].$$

The Si-atoms :

$$\left[\left[\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{5}{8}\right]\right] \quad \text{,,} \quad \left[\left[-\tfrac{1}{8}, -\tfrac{1}{8}, +\tfrac{3}{8}\right]\right].$$

The O-atoms :

$$\left.\begin{array}{c}\left[\left[\tfrac{1}{8}+\epsilon_1, \tfrac{1}{8}+\epsilon_1, \tfrac{1}{8}\right]\right], \quad \left[\left[\tfrac{1}{8}-\epsilon_1, \tfrac{1}{8}-\epsilon_1, \tfrac{1}{8}\right]\right] \\ \left[\left[-\tfrac{1}{8}+\epsilon_1, -\tfrac{1}{8}-\epsilon_1, -\tfrac{1}{8}\right]\right], \left[\left[-\tfrac{1}{8}-\epsilon_1, -\tfrac{1}{8}+\epsilon_1, -\tfrac{1}{8}\right]\right]\end{array}\right\}$$

connected to Zr.

$$\left.\begin{array}{c}\left[\left[\tfrac{1}{8}+\epsilon_2, \tfrac{1}{8}+\epsilon_2, \tfrac{5}{8}\right]\right], \quad \left[\left[\tfrac{1}{8}-\epsilon_2, \tfrac{1}{8}-\epsilon_2, \tfrac{5}{8}\right]\right] \\ \left[\left[-\tfrac{1}{8}+\epsilon_2, -\tfrac{1}{8}-\epsilon_2, \tfrac{3}{8}\right]\right], \quad \left[\left[-\tfrac{1}{8}-\epsilon_2, -\tfrac{1}{8}+\epsilon_2, \tfrac{3}{8}\right]\right]\end{array}\right\}$$

connected to Si.

To obtain the whole basis group of simple lattices we have merely to remember that to each coordinate $(x\,y\,z)$ correspond three other points with the coordinates :

$$(x+\tfrac{1}{2},\ y+\tfrac{1}{2},\ z),\quad (x+\tfrac{1}{2},\ y,\ z+\tfrac{1}{2}),\quad \text{and}\quad (x,\ y+\tfrac{1}{2},\ z+\tfrac{1}{2}).$$

Introducing the coordinates of the basis group into the general formula for the structure factor, we get after some reduction :

$$\begin{aligned} S = F[\cos A\{Zr + (-1)^{h_3}Si + O(\cos(h_1-h_2)\alpha_1 + \cos(h_1+h_2)\alpha_1 \\ + (-1)^{h_3}\cos(h_1-h_2)\alpha_2 + \cos(h_1+h_2)\alpha_2)\} \\ - iO\sin A\{\cos(h_1-h_2)\alpha_1 - \cos(h_1+h_2)\alpha_1 \\ + (-1)^{h_3}\cos(h_1-h_2)\alpha_2 - (-1)^{h_3}\cos(h_1+h_2)\alpha\}], \end{aligned} \quad . \ . \ . \quad (5)$$

where

$$A = \frac{\pi}{4}(h_1+h_2+h_3),$$

$$\alpha_1 = 2\pi\epsilon_1,$$

$$\alpha_2 = 2\pi\epsilon_2.$$

The chemical symbols stand for the atomic numbers.

The common factor F is the structure factor characteristic of the face-centred lattice :

$$F = [1 + (-1)^{h_2+h_3} + (-1)^{h_1+h_3} + (-1)^{h_1+h_2}].$$

Thus, if the indices $(h_1\,h_2\,h_3)$ are partly even and partly odd, $F \equiv O$ and the intensity of the corresponding line is zero.

As a matter of fact we see from Table II. that no line with mixed indices is observed, consequently the crystal of zircon is composed of *face-centred lattices.*

When the indices are either all even or all odd, $F = 4$.

We may therefore equally well drop the factor F and the equation (5) can be given the following simpler form :

$$\begin{aligned} S = \cos A[Zr + (-1)^{h_3}Si + 2O(\cos h_1\alpha_1 \cos h_2\alpha_1 \\ + (-1)^{h_3}\cos h_1\alpha_2 \cos h_2\alpha_2)] \\ - i2O\sin A\,(\sin h_1\alpha_1 \sin h_2\alpha_1 + (-1)^{h_3}\sin h_1\alpha_2 \sin h_2\alpha_2). \end{aligned} \quad . \ . \ . \quad (6)$$

We may distinguish between the following three cases :—

(*a*) $h_1+h_2+h_3=4n$; then $\cos A=\pm 1$, $\sin A=0$,

$$S=Zr+Si+2O(\cos h_1\alpha_1 \cos h_2\alpha_1+\cos h_1\alpha_2 \cos h_2\alpha_2).$$

(*b*) $h_1+h_2+h_3=4n\pm 1$; then $\cos A=\pm\frac{1}{\sqrt{2}}$, $\sin A=\pm\frac{1}{\sqrt{2}}$.

$$S=\frac{1}{\sqrt{2}}[Zr-Si+2O(\cos h_1\alpha_1 \cos h_2\alpha_1-\cos h_1\alpha_2 \cos h_2\alpha_2) \times i2O \operatorname{tg} A(\sin h_1\alpha_1 \sin h_2\alpha_1-\sin h_1\alpha_2 \sin h_2\alpha_2)].$$

(*c*) $h_1+h_2+h_3=4n+2$; then $\cos A=0$, $\sin A=\pm 1$.

$$S=2O(\sin h_1\alpha_1 \sin h_2\alpha_1+\sin h_1\alpha_2 \sin h_2\alpha_2).$$

The lines corresponding to case (*c*) are entirely due to the oxygen atoms, and the existence of lines of this group would show that the oxygen atoms cannot be arranged in lattices of the diamond type like Zr and Si. This is *e. g.* shown by the existence of a line with the indices (222) which was also found in my first investigations by means of the ionization method.

In the case of the lines of class (*a*) the wavelets from the Zr- and Si-atoms are in phase, while in the case of group (*b*) there is a phase difference of π, so the amplitudes are subtracted. The phase difference between waves from Zr- and Si-atoms depends on the actual displacement of the two lattices. The rule above mentioned is obtained from a displacement $c/2$ along the c-axis.

Now we find that all lines of group (*a*) are strong as compared with those of group (*b*), and this shows that we are right in assuming a mutual displacement of $c/2$.

If we introduce the parameters previously found,

$$\alpha_1=75°, \quad \alpha_2=30°,$$

we obtain an intensity distribution which has essential features in common with that observed, but there are some differences which indicate that the positions of the oxygen atoms are not quite correctly determined.

We have then tried to improve the agreement by taking other values of the parameters, and we obtain perhaps a somewhat better intensity distribution by putting

$$\alpha_1=60° \quad \text{and} \quad \alpha_2=45°.$$

The intensities calculated on this assumption are indicated by I_r and given in Table II. and in fig. 3.

Comparing these intensities with those observed I_0 (fig. 4 and Table II.), we notice that the calculated and observed intensities differ in a quite marked way for the lines No. 3,

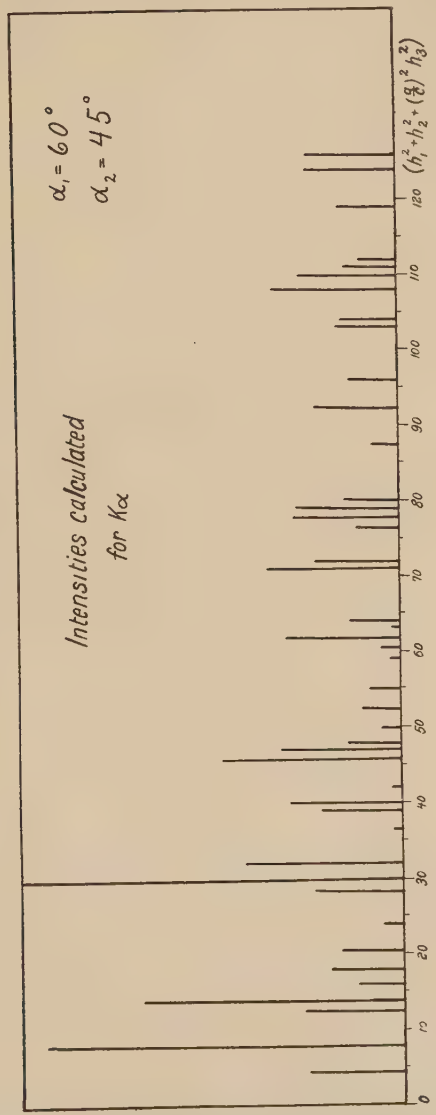


Fig. 3.

4, 5, 6 corresponding to (400), (222), (331), and (113). We may say that the calculated intensities of No. 3, 5, 6 come out too weak as compared with that of No. 4.

Further, the calculations give a too large intensity for the (311) line, which is too weak to be observed.

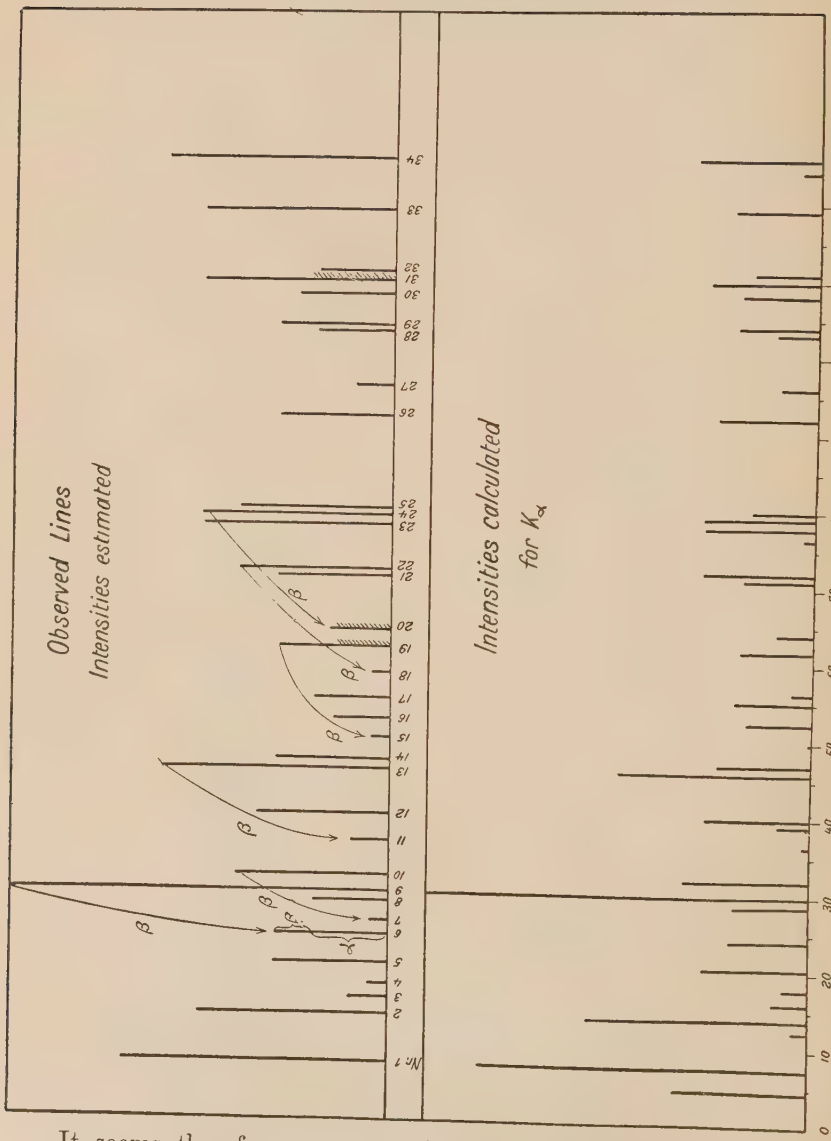


Fig. 4.
Zircon, $Zr\,Si\,O_4$

It seems therefore necessary in some way to introduce new parameters for the oxygen atoms.

Before proceeding further, we shall make a few remarks

regarding the symmetry of our lattices as compared with that found for the crystal.

According to P. Groth, 'Chemische Kristallographie,' zircon belongs to the ditetragonal-bipyramidal class.

Now the space lattice given for the Zr- and Si-atoms would give this symmetry, but when the arrangement proposed for the oxygen atoms is taken into account, there is no longer any reflecting plane perpendicular to the *c*-axis. The lattice corresponds to a ditetragonal-*pyramidal* crystal symmetry.

The space lattice belongs to the space group C_{4v}^{11}. This space group, however, has more parameters than introduced in our lattice. The space group C_{4v}^{11} is characterized by :

(1) Pseudo-diamond lattices movable along the *c*-axis.
(2) Point groups corresponding to the coordinate of the oxygen atoms and movable along the *c*-axis.

This point group gives in fact three new parameters, which do not disturb the symmetry, one parameter determining the displacement of the Si-atoms, and two parameters for the displacement of each of the two oxygen groups.

Now we saw, however, that the mutual displacement of Zr and Si is $c/2$, and this suggests that there probably may be found such positions for the oxygen atoms that the lattice will have a reflexion plane perpendicular to *c*.

If we call the displacement of the two oxygen groups $\eta_1 c$ and $\eta_2 c$, the arrangement of the oxygen atoms takes the form of a single group with bipyramidal symmetry, if we put

$$\epsilon_1 + \epsilon_2 = \tfrac{1}{4} \quad \text{and} \quad \eta_1 + \eta_2 = \tfrac{1}{4}.$$

If these conditions are fulfilled, we get only two parameters :

$$\epsilon = \epsilon_1 \qquad \text{and} \qquad \eta = \eta_1,$$

because we have

$$\epsilon = \tfrac{1}{4} - \epsilon \quad \text{and} \quad \eta_2 = \tfrac{1}{4} - \eta.$$

At the same time we pass over into the space group D_{4h}^{19} of higher symmetry. This is the same space group as found for anatase.

The construction points of the 8 face-centred lattices of the oxygen atoms have the coordinates :

$$\left[\left[\tfrac{1}{8}+\epsilon,\ \tfrac{1}{8}+\epsilon,\ \tfrac{1}{8}+\eta\right]\right], \quad \left[\left[\tfrac{1}{8}-\epsilon,\ \tfrac{1}{8}-\epsilon,\ \tfrac{1}{8}+\eta\right]\right],$$

$$\left[\left[\tfrac{1}{8}-\epsilon,\ \tfrac{1}{8}+\epsilon,\ \tfrac{1}{8}-\eta\right]\right], \quad \left[\left[\tfrac{1}{8}+\epsilon,\ \tfrac{1}{8}-\epsilon,\ \tfrac{1}{8}-\eta\right]\right],$$

$$\left[\left[-\tfrac{1}{8}-\epsilon,\ -\tfrac{1}{8}-\epsilon,\ -\tfrac{1}{8}-\eta\right]\right], \quad \left[\left[-\tfrac{1}{8}+\epsilon,\ -\tfrac{1}{8}+\epsilon,\ -\tfrac{1}{8}-\eta\right]\right],$$

$$\left[\left[-\tfrac{1}{8}+\epsilon,\ -\tfrac{1}{8}-\epsilon,\ -\tfrac{1}{8}+\eta\right]\right], \quad \left[\left[-\tfrac{1}{8}-\epsilon,\ -\tfrac{1}{8}+\epsilon,\ -\tfrac{1}{8}+\eta\right]\right].$$

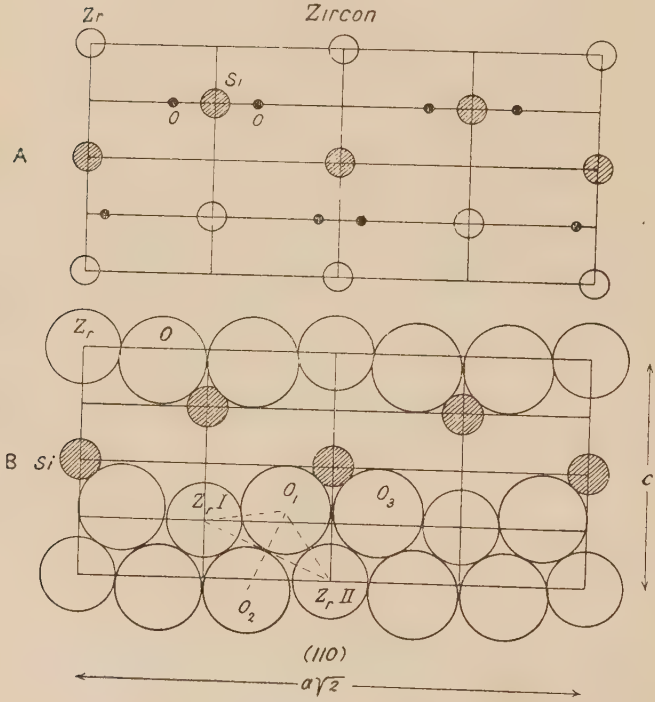
For the structure factor we deduce the formula:

$$S = \cos A\,(Zr + (-1)^{h_3} Si + 4O \cos h_1\alpha \cos h_2\alpha \cos h_3\gamma) + 4O \sin A \sin h_1\alpha \sin h_2\alpha \sin h_3\gamma. \quad (7)$$

We can now as before consider the cases (*a*), (*b*), (*c*) corresponding to

$$\Sigma h = 4n, \quad \Sigma h = 4n \pm 1, \quad \text{and} \quad \Sigma h = 4n + 2.$$

Fig. 5.



A *Old lattice of Zircon*
B *New* " " "

If in this formula we put

$$\alpha = 56° \quad \text{and} \quad \gamma = 20°,$$

and calculate the intensities by means of (7) and (3), we get the intensities I_{II} given in the last column of Table II.

Comparing the calculated and observed values, we notice

that the calculated intensities give the right type of variation throughout the whole spectrum *.

A point of great interest is that the relative intensities of the lines 3, 4, 5, 6 are now correct. The agreement between theory and observations is even better seen from fig. 4, where the calculated intensities are given underneath the observed ones.

In addition to the good representation of the intensities also comes that the modified lattice gives the right symmetry of the crystal, and I think there can be no doubt that we have found the right structure of zircon.

In this model all oxygen atoms are equal. Each atom of Zr or Si is surrounded by a group of four oxygen atoms, which are nearly placed at the corners of a tetrahedron. The structure corresponds to the formula $ZrSiO_4$.

The new position of the oxygen atoms is well illustrated if we consider the atoms in a (110) plane. The old and the new arrangements are shown in fig. 5.

Dimensions of the Atoms.

§ 4. We notice that each oxygen atom is situated near two Zr-atoms and one Si-atom. A simple calculation gives for the centre distances :

$$\rho_O + \rho_{Zr(I)} = 2{\cdot}10 \text{ Å}.$$

$$\rho_O + \rho_{Zr(II)} = 2{\cdot}22 \text{ ,,}$$

$$\rho_O + \rho_{Si} = 1{\cdot}72 \text{ ,,}$$

We see that the distances from the O-atom to the two Zr-atoms are very nearly equal. If we may regard the atoms as spheres in contact, the true value of the parameters ought to make the two centre distances equal.

As in the case of anatase we assume oxygen to exist in the form of negative ions O− −, with large diameters, and we are then led to consider the possibility that also the oxygen ions are in contact with each other. We shall have to consider distances between atoms like O_1-O_2 or O_1-O_3 (fig. 5 B),

* It should be remarked that the first of the calculated lines (111) is not found on the spectrogram on account of blackening of the film. The first order reflexion from (111), however, was found by means of the ionization method to be stronger than the following orders, and this is in agreement with the calculated intensities as seen from Table II.

and we find :

$$\text{Distance } O_1-O_2 = 2{\cdot}34 \text{ Å}.$$
$$\text{,, } \quad O_1-O_3 = 2{\cdot}43 \text{ ,,}$$

These distances are also approximately equal and of proper magnitude.

If now we regard the atoms as spheres in contact, the two parameters would be fixed without ambiguity by the two conditions of contact :

$$\text{Distance } Zr_{(I)}-O_1 = Zr_{(II)}-O_1,$$
$$\text{,, } \quad O_1-O_2 = O_1-O_3.$$

From these conditions we deduce the following equations :

$$\left.\begin{aligned} \epsilon-\frac{1}{2}\left(\frac{c}{a}\right)^2\eta &= \frac{1}{16}\left\{2+\left(\frac{c}{a}\right)^2\right\}, \\ \epsilon+\frac{1}{2}\left(\frac{c}{a}\right)^2(\eta+4\eta^2) &= \frac{1}{16}\left\{3-\frac{1}{2}\left(\frac{c}{a}\right)^2\right\}, \end{aligned}\right\} \quad \cdot \cdot \quad (8)$$

which give

$$\epsilon = 0{\cdot}161, \qquad \alpha = 58°{\cdot}0,$$
$$\eta = 0{\cdot}0535, \qquad \gamma = 19°{\cdot}3.$$

These parameters give :

$$\text{Minimum centre distance } O-O = 2{\cdot}36 \text{ Å},$$
$$\text{,, } \quad \text{,, } \quad \text{,, } \quad Zr-O = 2{\cdot}17 \text{ ,,}$$
$$\text{,, } \quad \text{,, } \quad \text{,, } \quad Si-O = 1{\cdot}67 \text{ ,,}$$

and for the ionic dimensions :

$$\rho_O = 1{\cdot}18 \text{ Å},$$
$$\rho_{Zr} = 0{\cdot}99 \text{ ,,}$$
$$\rho_{Si} = 0{\cdot}49 \text{ ,,}$$

The radius here found for the oxygen atoms is very nearly the same as the radius found in the case of anatase. The contact conditions in the (110) plane gave in that case $\rho_O = 1{\cdot}24$ Å.

The structure of zircon regarded as formed by spheres of the dimensions here given is a most compact one. This will be seen from fig. 5 B. The apparent gap is filled by atoms having their centres outside the plane of the drawing.

III. Rutile and Cassiterite. TiO_2 and SnO_2.

§ 5. Like zircon, the crystals of rutile and cassiterite belong to the ditetragonal-bipyramidal class.

The ratios c/a are for zircon 0·6391, for rutile 0·6439, and for cassiterite 0·6726. The three minerals were therefore regarded as isomorphous.

In my previous investigations I found that the lattice of rutile and cassiterite could be obtained from the zircon lattice by specifying the values of the parameters. As, however, Zr and Si were replaced by equal atoms, this substitution increased the symmetry in the way that the lattice of rutile and cassiterite got reflexion planes perpendicular to the c-axis. To put it short, through the substitution the lattice passed over from the space group C_{4v}^{11} to the group D_{4h}^{14}.

Now we found, however, that the zircon lattice had to be slightly modified with regard to the position of the oxygen atoms. By a proper choice of oxygen parameters we were able to raise the symmetry from that of the space group C_{4v}^{11} to that of D_{4h}^{19}, and in this way we obtained the right zircon structure.

It is now a question of considerable importance to know whether the lattices of rutile and cassiterite can be derived by specifying the parameters of the zircon lattice, or whether they have the structure which was found in my first investigations. In the latter case zircon will not be exactly isomorphous with the two other minerals.

The lines of the spectra and the usual data concerning intensities and identifications of lines are given in Tables III. and IV. for rutile and cassiterite respectively.

We shall first consider the lattice which was previously found by means of the ionization method.

The structure factor is found from (5) by putting $\alpha_1=\alpha_2=\alpha$ and substituting Zr and Si with Ti resp. Sn. Then we get

$$S=(1+(-1)^{h_3})\big[\cos A\{M+2O\cos h_1\alpha\cos h_2\alpha\} + i\,2O\sin A\sin h_1\alpha\sin h_2\alpha\big], \quad (9)$$

where M is the atomic number of the metal Ti or Sn.

TABLE III.—Rutile, Ti_2O_4.

$a = 9{\cdot}30$ Å. $c = 5{\cdot}98$ Å. $c/a = 0{\cdot}643$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
1	12·28	$(8{\cdot}05)_\beta$	(8·00)	(2.2.0)		
2	13·53	8·00	8·00	2.2.0	76	50
3	16·15	$(13{\cdot}76)_\beta$	(13·64)	(2.0.2)		
4	17·87	13·74	13·64	2.0.2	47	30
5	19·33	16·01	16·00	4.0.0	5	5
6	20·38	17·70	17·64	2.2.2	30	20
7	21·79	20·12	20·00	4.2.1	9	10
8	23·88	$(29{\cdot}18)_\beta$	(29·64)	(4.2.2)		
9	24·98	$(31{\cdot}77)_\beta$	(32·00)	(4.4.0)		
10	26·80	$29{\cdot}68)_\beta$	29·64	4.2.2	100	100
11	27·85	31·88	32·00	4.4.4	36	40
12	30·41	$(45{\cdot}64)_\beta$	(45·64)	(6.0.2)		
13	33·93	38·58	38·58	0.0.4	20	10
14	31·56	40·00	40·00	6.2.0	18	10
			41·64	4.4.2	0	
15	34·01	45·67	45·64	6.0.2	59	70
			46·58	2.2.4	26	
			49·64	6.2.2	0	
			52·00	6.4.0	0	
			54·58	4.0.4	3	
			58·58	4.2.4	0	
16	40·60	61·84	61·64	6.4.2	9	10
17	41·43	63·92	64·00	8.0.0	12	10
			68·00	8.2.0	0	
18	44·10	70·71	70·58	4.4.4	33	25
19	44·83	72·57	72·00	6.6.0	16	10
			77·64	8.2.2	24	
20	47·18	78·54	78·58	6.4.2	18	20
21	47·91	80·40	80·00	8.4.0	9	5
			81·64	6.6.2	0	
22	50·98	$(106{\cdot}91)_\beta$	(106·80)	(4.2.6)		
			89·64	8.4.2	0	
23	52·15	90·95	90·80	2.0.6	7	10
			90·58	6.4.4	0	
			94·80	2.2.6	0	
24	56·90	102·45	102·58	8.0.4	15	10
25	57·53	103·94	104·00	10.2.0	15	10
26	59·15	107·62	106·80	4.2.6	28	40
			106·58	8.2.4	0	
			109·64	8.6.2	28	
27	60·56	110·73	109·64	10.0.2		50
			110·58	6.6.4	32	
			113·64	10.2.2	0	
			116·00	10.4.0	0	
28	64·89	119·66	118·58	8.4.4	12	10
			118·80	4.4.6	0	
29	66·98	123·68	122·80	6.0.6	22	30
30	68·80	126·92	125·64	10.4.2	43	50

TABLE IV.—Cassiterite, Sn_2O_4.

$a = 9{\cdot}45$ Å. $c = 6{\cdot}36$ Å. $c/a = 0{\cdot}673$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
1	13·43	8·13	8·00	2.2.0	82	60
2	15·41	$(13{\cdot}09)_\beta$	(12·84)	(2.0.2)		
3	17·09	13·02	12·84	2.0.2	82	80
4	19·07	16·09	16·00	4.0.0	22	20
			16·84	2.2.2	7	
			20·00	4.2.0	2	
5	23·30	$(29{\cdot}00)_\beta$	(28·84)	(4.2.2)		
6	24·61	$(32{\cdot}15)_\beta$	(32·00)	(4.4.0)		
7	26·02	29·00	28·84	4.2.2	100	100
8	27·54	32·33	32·00	4.4.0	28	30
9	29·00	35·43	35·36	0.0.4	15	15
10	29·52	$(44{\cdot}99)_\beta$	(44·84)	(6.0.2)		
11	31·04	40·08	40·00	6.2.0	27	30
			40·84	4.4.2	0	
12	32·50	43·52	43·63	2.2.4	31	30
13	33·13	45·03	44·84	6.0.2	44	40
			48·84	6.2.2	2	
14	35·84	51·68	51·36	4.0.4	14	20
			52·00	6.4.0	0	
			55·36	4.2.4	2	
15	39·50	60·99	60·84	4.6.2	27	35
16	40·65	63·97	64·00	8.0.0	12	15
17	42·01	67·50	67·36	4.4.4	27	30
			68·00	8.2.0	2	
18	43·68	71·89	72·00	6.6.0	13	15
19	44·94	75·22	75·36	6.2.4	28	35
20	45·61	77·00	76·84	8.2.2	32	40
21	46·76	80·00	80·00	8.4.0	14	20
			80·84	6.6.2	0	
22	48·28	83·95	83·56	2.0.6	12	15
			87·36	6.4.4	0	
			87·56	2.2.6	1	
			88·84	8.4.2	1	
23	50·11	$(109{\cdot}18)_\beta$	(108·84)	(8.6.2)		
24	52·20	$(115{\cdot}77)_\beta$	(115·36)	(8.4.4)		
			99·56	4.2.6	44	50
25	54·34	99·50				
			99·36	8.0.4		
			103·36	8.2.4	2	
26	56·12	103·90	104·00	10.2.0	15	15
27	57·58	107·41	107·36	6.6.4	17	20
			108·84	10.0.2	31	40
28	58·21	108·88				
			108·84	8.6.2		
			111·56	4.4.6	0	
			112·84	10.2.2	0	
			115·56	6.0.6	35	50
29	61·03	115·37				
			115·36	8.4.4		
			119·56	6.2.6	1	
30	65·31	124·41	124·84	10.4.2	35	50
31	66·93	127·60	128·00	8.8.0	5	15
32	69·02	131·42	131·56	6.4.6	12	40
			135·36	8.6.4	0	
33	71·34	135·44	136·03	10.6.0	5	20
			136·84	8.8.2	1	
34	73·72	138·90	139·36	10.2.4	21	50

Remembering that all reflexions from faces with mixed indices vanish, we see that faces with odd indices give no

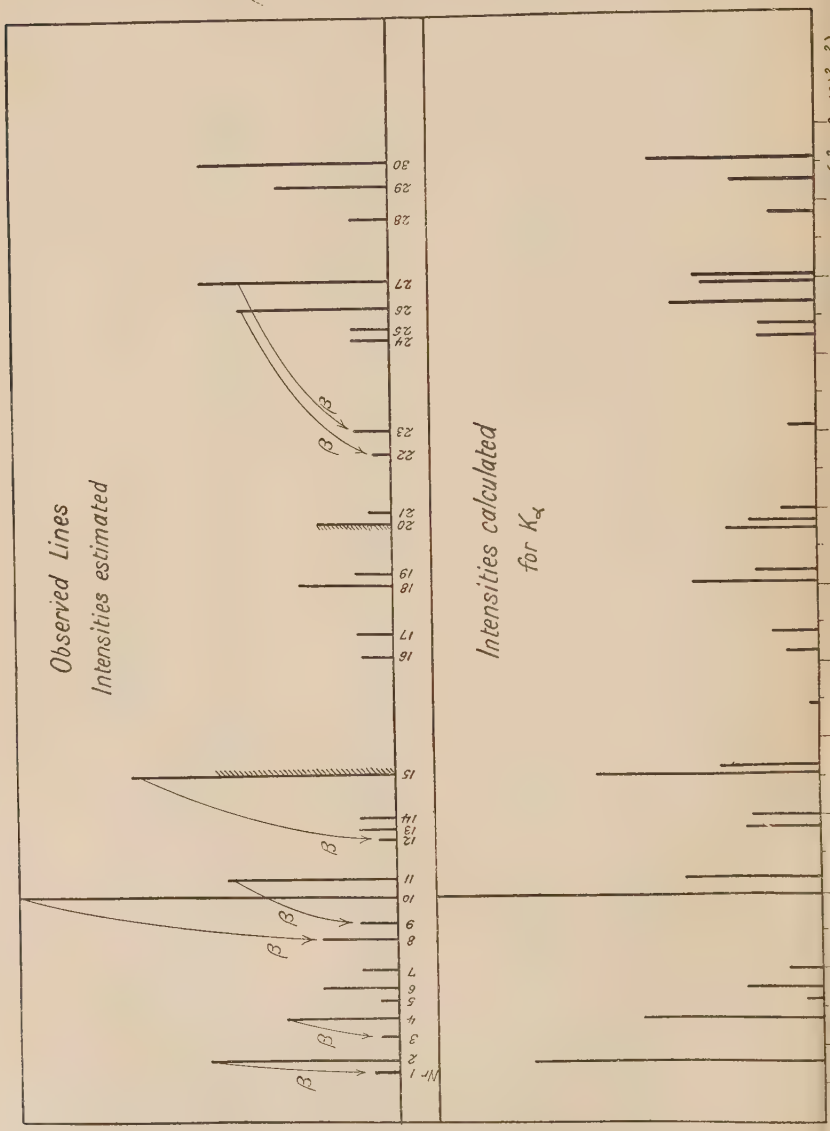


Fig. 6.

reflexion, because $(1+(-1)^{h_3})=0$. We may also say that faces for which $\Sigma h=4n\pm1$ give no reflexion.

This is also in accordance with observations. We have

therefore only to consider the two cases:

(1) $\Sigma h = 4n$, $\quad S = M + 2O \cos h_1\alpha \cos h_2\alpha$;

(2) $\Sigma h = 4n+2$, $\quad S = 2O \sin h_1\alpha \sin h_2\alpha$.

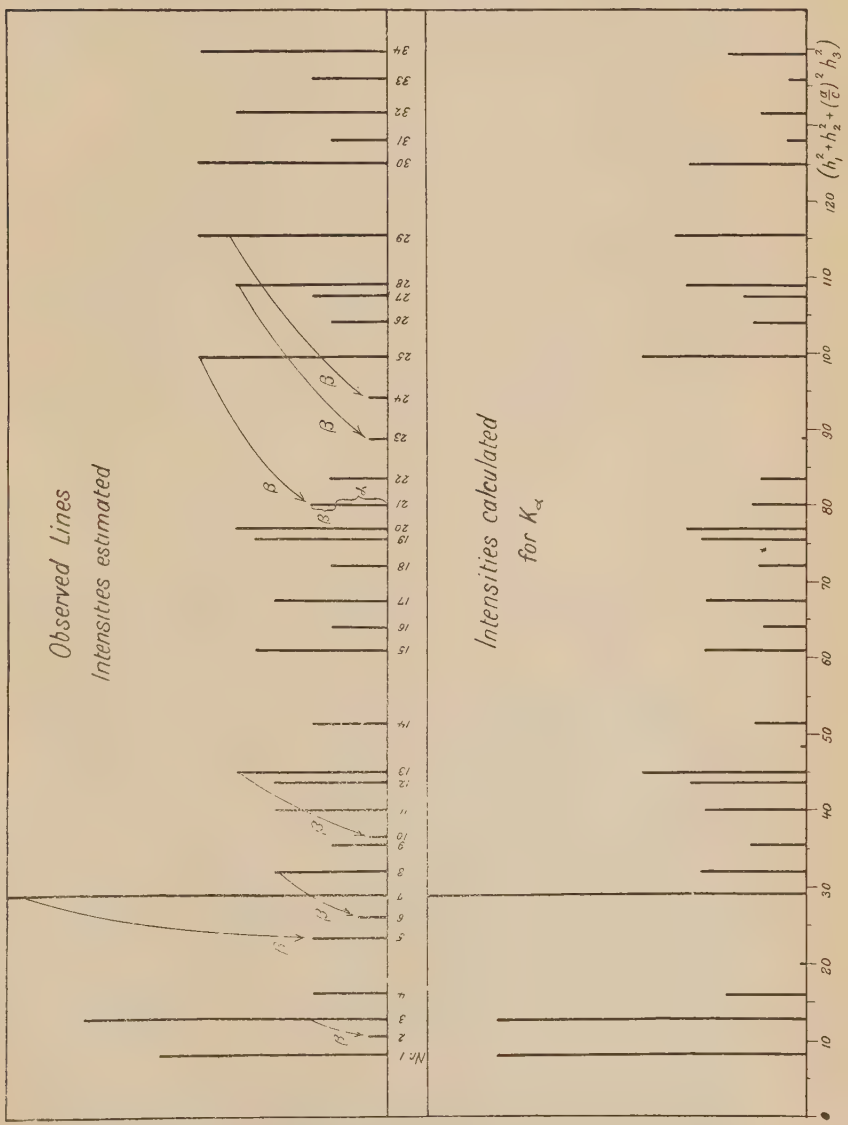


Fig. 7.

As the lines of the second group result only from the O atoms, these lines must as a rule be weak as compared with those of the first group.

As a matter of fact, we find that the lines of the first group dominate the spectrum.

In the case of SnO_1 the reflexion from Sn is so dominating that only lines of the first group appear, Rutile, however, shows the lines (222) and (420) corresponding to case (2).

The parameters originally found were:

For rutile, $\alpha = 55°{\cdot}75$.

For cassiterite, $\alpha = 56°{\cdot}25$.

We have here calculated the intensities by putting $\alpha = 54°$ for both minerals.

The intensities calculated in this way are given in the Tables III. and IV. and graphically represented in figs. 6 and 7. The agreement between the observed and calculated intensity distribution is seen to be remarkably good.

If on the other hand we would apply the zircon lattice, we come into conflict with observed facts.

The structure factor derived from that of zircon takes the form:

(1) $\Sigma h = 4n$, $\quad S = \mathrm{Ti} + 2O \cos h_1\alpha \cos h_2\alpha \cos h_3\gamma$,

(2) $\Sigma h = 4n+2$, $\quad S = 2O \sin h_1\alpha \sin h_2\alpha \sin h_3\gamma$,

(3) $\Sigma h - 4n \pm 1$, $\quad S = \frac{1}{\sqrt{2}} 2O \left\{ \begin{matrix} \cos h_1\alpha \cos h_2\alpha \cos h_3\gamma \\ + \sin h_1\alpha \sin h_2\alpha \sin h_3\gamma \end{matrix} \right\}$.

In this case lines of odd indices should appear, but no line of this group is observed. It might be argued, however, that these lines were merely too faint to show up on the film. It is therefore also of special importance to consider the lines (222) and (420). They are both observed, but according to the above formula (case 2) the line (420) should vanish because $\sin h_3\gamma = 0$.

On account of the space filling conditions γ must be very small, and the above formula would therefore give an intensity for the (222) line which is too small to explain its appearance on the film.

We therefore conclude that *the structure originally found for rutile and cassiterite is right*, and these minerals *with a space group* D_{4h}^{14} *are not exactly isomorphous with zircon with a space group* D_{4h}^{19}.

The considerable difference between the structure of zircon and that of rutile and cassiterite will be seen by

comparing fig. 5 and fig. 8, giving the atomic arrangements in the (110) planes for these minerals. The difference is also

Fig. 8.

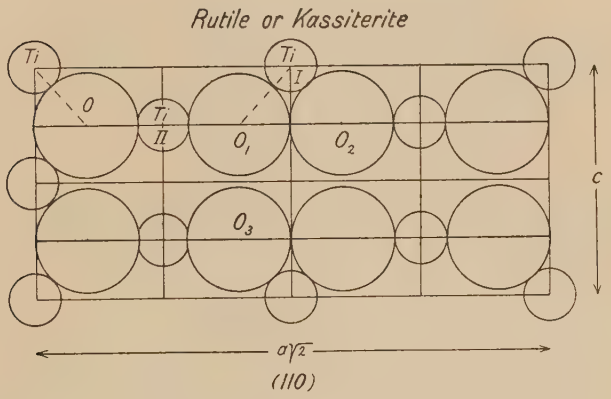
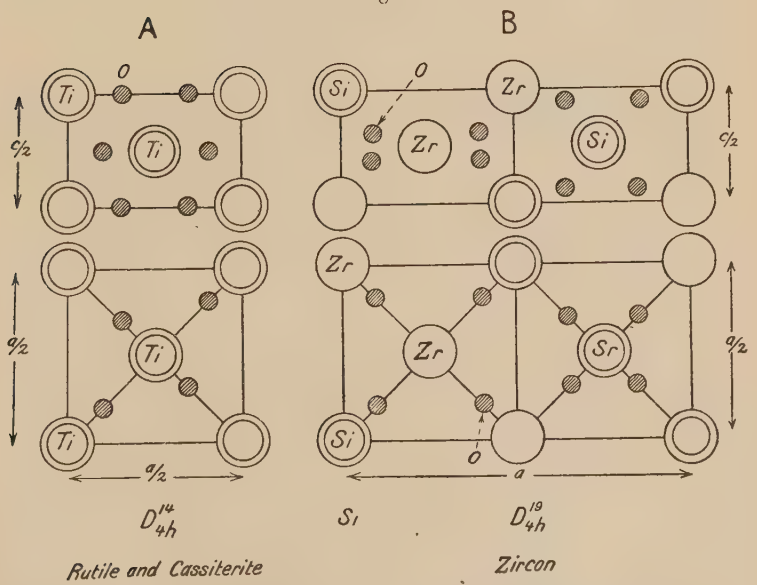


Fig. 9.



clearly seen by comparing fig. 9 A and fig. 9 B, giving the horizontal and vertical projection of the two lattices.

Dimensions of the Atoms.

§ 6. From fig. 8 we easily deduce the distance from the O-centres to those of the nearest Ti- resp. Sn-atoms.

For rutile,

$$\rho_O + \rho_{Ti}(I) = 1{\cdot}97 \text{ Å}.$$
$$\rho_O + \rho_{Ti}(II) = 1{\cdot}99 \text{ ,,}$$

For cassiterite,

$$\rho_O + \rho_{Sn}(I) = 2{\cdot}00 \text{ Å}.$$
$$\rho_O + \rho_{Sn}(II) = 2{\cdot}08 \text{ ,,}$$

The two centre distances are very nearly equal. We can, as before, find such parameters as will make them exactly equal.

From these conditions we get for the parameters :

For rutile,

$$\epsilon = 0{\cdot}151, \qquad \alpha = 54^{\circ}{\cdot}3.$$

For cassiterite,

$$\epsilon = 0{\cdot}153, \qquad \alpha = 55^{\circ}{\cdot}2.$$

Applying these parameter values, the minimum centre distance for two oxygen atoms like O_1 and O_2, fig. 8, will be :

For rutile, $O_1 - O_2 = 2{\cdot}62$ A.

For cassiterite, ,, $= 2{\cdot}60$,,

If we consider these oxygen atoms to be spheres in contact, we can find the following dimensions for the spherical ions :

Rutile, $\rho_O = 1{\cdot}31$ Å., $\rho_{Ti} = 0{\cdot}67$ Å.

Cassiterite, $\rho_O = 1{\cdot}30$,, $\rho_{Sn} = 0{\cdot}75$,,

TABLE V.

Substance.	Space group.	Dimensions of elementary lattice.		Parameters.		Radius of ions.	
		a.	*c*.	ϵ.	η.	Negative (oxygen).	Positive.
Anatase	D_{4h}^{19}	5·37 Å.	9·54 Å.	.....	0·204	1·32 Å.	Ti 0·63 Å.
Rutile	D_{4h}^{14}	9·30 ,,	5·98 ,,	0·151	.....	1·31 ,,	Ti 0·67 ,,
Cassiterite ...	,,	9·45 ,,	6·36 ,,	0·153	.....	1·30 ,,	Sn 0·75 ,,
Zircon	D_{4h}^{19}	9·41 ,,	6·01 ,,	0·161	0·0535	1·18 ,,	Zr 0·99 ,,
							Si 0·49 ,,

For the sake of comparison the constants of the lattices of the minerals anatase, zircon, rutile, and cassiterite are collected in Table V.

IV. The Structure of the Scheelite Group.

§ 7. The crystals of the mineral Scheelite belong to the tetragonal-bipyramidal class. Isomorphous with scheelite we have a number of other minerals like

$CaMoO_4$ (powellite),
$BaWO_4$,
$BaMoO_4$,
$PbWO_4$,
$PbMoO_4$.

With regard to chemical formula, these minerals bear some resemblance to zircon $ZrSiO_4$, but the crystal form differs both as regards symmetry, class, and axis ratio c/a, which in the case of the scheelite group is about 3/2, while for zircon c/a was only 0·64.

An analysis of the scheelite group was commenced in 1916 by means of the ionization method, and for scheelite itself the following results were obtained :

The elementary lattice contained 8 molecules $CaWO_4$. The side of the base was found to be $a=7{\cdot}48$ Å. and the height $c=11{\cdot}3$ Å. It was further found that both the Ca- and W-atoms were arranged in pseudo-cubic lattices of the diamond type displaced relative to each other a distance $c/2$ in the direction of the c-axis.

Any definite result regarding the arrangement of the oxygen atoms was not obtained at that time. The expansion of the lattice in the c-direction would suggest that the oxygen atoms were similarly arranged as for anatase, in such a way that Ca and W formed centres of a group O–W–O with its axis in the c-direction. This arrangement, however, gave no satisfactory agreement with observations.

In order to determine accurately the positions of the oxygen atom, spectrograms after the method of Debye-Scherrer were taken, to begin with only for the minerals scheelite and powellite ; but later on the investigations were extended to other members of the group.

The knowledge already gained by means of the Bragg method was sufficient for the interpretation of the lines on the spectrogram.

In Tables VI. and VII. are given the observed lines. The first column contains the current number of the lines in the

order of increasing reflexion-angle ϕ, given in the second column.

TABLE VI.—Scheelite, $CaWO_4$.

$a=7{\cdot}44$ Å. $c=11{\cdot}35$ Å. $c/a=1{\cdot}537$.
$\alpha=20°$. $\beta=20°$. $\gamma=72°$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
			2·43	1.1.1	28	
1	12·91	$(5{\cdot}72)_\beta$	(5·72)	(2.0.2)		
			5·72	2.0.2	100	100
2	14·37	5·75				
			5·86	1.1.3		
3	15·52	6·68	6·86	0.0.4	26	10
4	17·09	8·06	8·00	2.2.0	40	35
5	19·44	10·33	10·43	3.1.1	19	25
6	21·26	$(15{\cdot}08)_\beta$	(14·86)	(2.2.4)		
			12·73	1.1.5	2	
7	22·52	13·68	13·86	3.1.3	16	10
8	23·56	14·80	14·86	2.2.4	39	50
9	24·56	16·11	16·00	4.0.0	18	30
10	25·94	$(21{\cdot}80)_\beta$	(21·72)	(4.2.2)		
			18·43	3.3.1	6	
11	27·22	19·29	19·44	2.0.6	33	35
12	28·00	20·57	20·73	3.1.5	8	10
			21·72	4.2.2		
13	28·95	21·84			66	60
			21·86	3.3.3		
			22·86	4.0.4		
14	29·68	22·86			33	30
			23·02	1.1.7		
15	32·29	26·60	26·43	5.1.1	9	15
			27·46	0.0.8	4	
16	33·75	28·79	28·73	3.3.5	5	15
17	34·49	29·91	29·86	5.1.3	6	10
18	35·22	31·02	31·02	3.1.7	7	10
19	35·95	32·15	32·00	4.4.0	4	10
			34·43	3.5.1	7	
			35·44	4.2.6		
20	38·40	35·41			44	55
			35·46	2.2.8		
			36·73	5.1.5		
					8	
			36·75	1.1.9		
			37·72	6.0.2		
21	39·55	37·81			22	25
			37·86	5.3.3		
			38·86	4.4.4		
22	40·25	38·93			13	15
			39·02	3.3.7		
23	41·17	40·42	40·00	6.2.0	13	15
24	43·21	43·40	43·46	4.0.8	13	20
			44·73	5.3.5		
25	43·94	44·93			13	10
			44·75	3.1.9		

TABLE VI. (*continued*).

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
			46·86	6.2.4		
26	45·20	46·95			44	50
			46·90	2.0.10		
			47·02	5.1.7		
			50·43	5.5.1		
					6	
			50·43	7.1.1		
27	47·88	51·29	51·44	6.0.6	12	15
			52·75	3.3.9	2	
			53·72	6.4.2		
			53·86	5.5.3		
28	49·48	53·89			33	40
			53·86	7.1.3		
			53·91	1.1.11		
			55·02	5.3.7	1	
			58·43	7.3.1	3	
29	52·77	59·14	59·46	4.4.8	15	10
			60·73	7.1.5		
30	53·92	60·03	60·73	5.5.5	10	15
			60·75	5.1.9		
			61·78	0.0.12		
			61·86	7.3.3	7	
			61·91	3.1.11		
31	55·18	62·87	62·90	4.2.10	14	20
32	56·22	63·96	64·00	8.0.0	8	5
			67·44	6.2.8		
33	58·31	67·54			33	50
			67·46	6.4.6		
			68·73	7.3.5		
					7	
			68·75	5.3.9		
			69·78	2.2.12		
34	59·88	69·77	69·72	8.2.2	21	30
			69·91	3.3.11		
			70·86	8.0.4		
35	60·98	71·32	71·02	5.5.7	13	25
			71·02	7.1.7		
			72·00	6.6.0	3	
36			74·43	7.5.1	3	10
			77·78	4.0.12		
37	65·68	77·44	77·86	7.5.3	12	25
			77·91	5.1.11		
			78·86	6.6.4		
38	66·83	78·83	78·90	6.0.10	17	30
			79·02	7.3.7		
39	67·85	80·10	80·00	8.4.0	7	10
			82·43	9.1.1	2	
40	70·90	83·92	83·44	8.2.6	12	30
			84·75	5.5.9		
			84·75	7.1.9	7	
			84·73	7.5.5		
			85·86	9.1.3		
					7	
			85·91	5.3.11		
41	75·03	87·07	86·86	8.4.4	13	40

TABLE VII.—Powellite, $CaMoO_4$.

$a = 7{\cdot}40$ Å. $c = 11{\cdot}44$ Å. $c/a = 1{\cdot}546$.
$\alpha = 20°$. $\beta = 20°$. $\gamma = 72°$.

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{c}{a}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
			2·42	1.1.1	7	
1	13·17	$(5{\cdot}90)_\beta$	(5·67)	(2.0.2)		
			5·67	2.0.2		
2	14·32	5·65			100	100
			5·77	1.1.3		
3	15·62	6·70	6·70	0.0.4	37	10
4	17·19	8·08	8·00	2.2.0	52	30
5	19·44	10·24	10·42	3.1.1	15	15
6	21·00	$(14{\cdot}60)_\beta$	(14·70)	(2.2.4)		
			12·47	1.1.5	0	
			13·77	3.1.3	11	
7	23·51	14·70	14·70	2.2.4	51	60
8	24·56	15·97	16·00	4.0.0	23	30
9	25·86	$(21{\cdot}63)_\beta$	(21·67)	(4.2.2)		
			18·42	3.3.1	4	
10	26·96	19·01	19·07	2.0.6	45	40
			20·47	3.1.5	3	
			21·67	4.2.2		
11	29·00	21·73			88	70
			21·77	3.3.3		
			22·70	4.0.4		
12	29·68	22·67			39	20
			22·51	1.1.7		
13	32·39	26·62	26·42	5.1.1	8	10
			26·80	0.0.8	2	
14	33·70	28·45	28·47	3.3.5	5	10
			29·77	5.1.3	4	
15	34·95	30·18	30·51	3.1.7	5	10
16	36·52	32·74	32·00	4.4.0	3	10
			34·42	3.5.1		
17	37·93	34·94	34 80	2.2.8	59	90
			35 07	4.2.6		
			35·91	1.1.9	0	
			36·47	5.1.5	3	
			37·67	6.0.2		
18	39·71	37·74			23	30
			37·77	5.3.3		
			38·51	3.3.7		
					13	
			38·70	4.4.4		
19	41·12	39·99	40·00	6.2.0	15	20
20	42·74	42·58	42·80	4.0.8	16	10
			43·91	3.1.9	3	
			44·47	5.3.5	8	
			45·86	2.0.10	26	
21	45·09	46·38	46·51	1.5.7	24	60
			46·70	6.2.4		

TABLE VII. (*continued*).

No.	$\phi°$.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$\left(h_1^2+h_2^2+\left(\frac{c}{a}\right)^2 h_3^2\right)$.	$h_1h_2h_3$.	I.	
					cal.	obs.
			50·42	5.5.1	3	
			50·42	7.1.1		
22	47·91	50·91	51·07	6.0.6	15	30
			51·91	3.3.9	1	
			52·65	1.1.11	0	
			53·67	6.4.2	38	50
23	49·64	53·67	53·77	5.5.3		
			53·77	7.1.3		
			54·51	5.3.7	0	
			58·42	7.3.1	2	
24	52·67	58·48	58·80	4.4.8	23	10
			59·91	5.1.9	5	
			59·98	0.0.12		
25	53·82	60·25	60·47	5.5.5	4	10
			60·47	7.1.5		
26	54·86	61·83	61·86	4.2.10	15	30
27	56·12	63·71	64·00	8.0.0	12	5
			66·80	6.2.8	41	80
28	58·15	66·70	67·07	6.4.6		
			67·91	5.3.9	11	
			67·98	2.2.12		
			68·47	7.3.5	3	
			68·65	3.3.11	0	
			69·67	8.2.2	13	
29	60·24	69·66	70·51	5.5.7	16	50
			70·51	7.1.7		
			70·70	8.0.4		
			72·00	6.6.0	3	
			74·42	7.5.1	2	
			75·98	4.0.12	12	20
30	65·10	76·06	76·65	5.1.11		
			77·77	7.5.3	12	20
31	66·77	78·07	77·86	6.0.10		
			78·51	7.3.7	8	
			78·70	6.6.4		
32	68·45	80·00	80·00	8.4.0	8	20
			82·42	9.1.1	15	60
33	71·16	82·81	83·07	8.2.6		
			83·91	5.5.9	2	
			83·91	7.1.9		
			84·47	7.5.5	5	
			84·65	5.3.11		
			85·77	9.1.3	4	
34	75·08	86·32	86·70	8.4.4	17	30

The correctness of the identification of lines is seen from columns 3 and 4. The fifth column gives the indices of the lines, and the last two columns give observed and calculated intensities.

At the head of each table are given the dimensions of the lattice and the values of the parameters used for calculating the intensities. We shall see later on that these parameters must probably be slightly modified to suit the space-filling conditions of the atoms.

Symmetry of the Lattice.

§ 8. The arrangement of the metal atoms was found by the Bragg method, and this result was confirmed by the Debye-Scherrer spectrograms. If we look at the structure apart from the oxygen atoms, the lattice of Ca and W in scheelite has exactly the same symmetry as that of Zr and Si in zircon—both belong to the space group D_{4h}^{19}.

In the case of zircon also the oxygen atoms were arranged in accordance with this space group. Scheelite, however, has the lower symmetry of the tetragonal-bipyramidal class, and if this degradation of symmetry is not due to an asymmetry of the centres, we are led to suppose that the oxygen atoms are arranged in a space group which has no reflexion plane parallel to the (110) plane.

The symmetry elements parallel to the *c*-axis, which are characteristic of the lattice of Ca–W (space group D_{4h}^{19}) are illustrated in fig. 10. There is one system of right screw axis, one of left screw axis, and one system of diagonal axis.

Parallel to (110) are reflexion planes (drawn in full) and gliding reflexion planes (dotted lines). Parallel to (100) are gliding reflexion planes (dotted).

The arrangement of Ca- and W-atoms around one of the screw axes is shown in fig. 11.

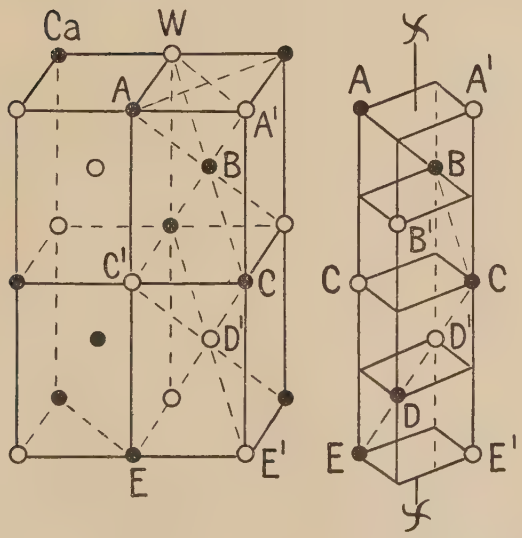
In addition, the lattice has gliding reflexion planes perpendicular to the *c*-axis. The planes $(001)_{1/8}$ and $(001)_{5/8}$ with gliding components $\frac{a_x}{4}+\frac{a_y}{4}$ and the planes $(001)_{3/8}$ and $(001)_{7/8}$ with gliding components $\frac{a_x}{4}-\frac{a_y}{4}$.

When we take into account the oxygen atoms, the lattice loses the symmetry planes parallel to the *c*-axis, but we assume the tetragonal screw axis and the horizontal reflexion planes to be preserved. The lattice then corresponds to the space group C_{4h}^{6}.

The lattice containing 8 molecules must contain 32 oxygen atoms.

Fig. 10.

Fig. 11.



The space group gives two groups of eight points without degrees of freedom. These positions are occupied by the Ca- and W-atoms. The space group gives further two

groups of sixteen points without degrees of freedom and one group of sixteen with one degree of freedom. An arbitrary point with three parameters has 32 equivalent positions. If, therefore, the oxygen atoms are to be arranged according to C_{4h}^{6}, we must either divide them in two groups of 16 or in one group of 32 with three parameters. Only the last arrangement can explain the symmetry of the crystal.

Structure Factor and Intensities.

§ 9. We place the coordinate system with the axis parallel to a and c and with the origin at the centre of one of the Ca-atoms. Let the coordinates of one O-atom be :

$$x = la,$$
$$y = ma,$$
$$z = nc.$$

The coordinates of the other 31 atoms are then found by applying the symmetry conditions of the lattice. We then find that the oxygen atoms may be regarded as arranged in 8 face-centred lattices.

Taking the symmetry centre $(\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8})$ as origin of the coordinate system, the positions of the 8 face-centred lattices are given by the coordinates :

$$\left[\left[\tfrac{1}{8}+l,\ \tfrac{1}{8}+m,\ \tfrac{1}{8}+n\right]\right],\quad \left[\left[\tfrac{1}{8}-l,\ \tfrac{1}{8}-m,\ \tfrac{1}{8}+n\right]\right],$$
$$\left[\left[\tfrac{1}{8}+m,\ \tfrac{1}{8}-l,\ \tfrac{1}{8}-n\right]\right],\quad \left[\left[\tfrac{1}{8}-m,\ \tfrac{1}{8}+l,\ \tfrac{1}{8}-n\right]\right],$$
$$\left[\left[-\tfrac{1}{8}-l,\ -\tfrac{1}{8}-m,\ -\tfrac{1}{8}-n\right]\right],\quad \left[\left[-\tfrac{1}{8}+l,\ -\tfrac{1}{8}+m,\ -\tfrac{1}{8}-n\right]\right],$$
$$\left[\left[-\tfrac{1}{8}-m,\ -\tfrac{1}{8}+l,\ -\tfrac{1}{8}+n\right]\right],\quad \left[\left[-\tfrac{1}{8}+m,\ -\tfrac{1}{8}-l,\ -\tfrac{1}{8}+n\right]\right].$$

The structure factor of the oxygen atoms :

$$\frac{S}{O} = 2F\left[\cos 2\pi\left(\frac{\Sigma h}{8}+h_1 l+h_2 m+h_3 n\right)\right.$$
$$+\cos 2\pi\left(\frac{\Sigma h}{8}-h_1 l-h_2 m+h_3 n\right)$$
$$+\cos 2\pi\left(\frac{\Sigma h}{8}+h_1 m-h_2 l-h_3 n\right)$$
$$\left.+\cos 2\pi\left(\frac{\Sigma h}{8}-h_1 m+h_2 l-h_3 n\right)\right],\quad .\quad .\quad (10)$$

where

$$F = 1+(-1)^{h_2+h}+(-1)^{h_1+h_3}+(-1)^{h_1+h_2}$$

is the structure factor of the face-centred lattice, which

is $=0$ for mixed indices. When the indices are either all even or all odd, $F=4$. This consequence is so far in agreement with observations, because no line corresponding to mixed indices appears on the spectrogram.

We put

$$\frac{\pi}{4}(h_1+h_2+h_3) = A,$$

$$2\pi l = \alpha+\beta, \quad \alpha = 2\pi\frac{l+m}{2},$$

$$2\pi m = \alpha-\beta, \quad \beta = 2\pi\frac{l-m}{2},$$

$$2\pi n = \gamma.$$

Excluding the cases of mixed indices for which $S=0$, we get:

$$\begin{aligned}\frac{S}{8O} = &\cos[A+h_1(\alpha+\beta)+h_2(\alpha-\beta)+h_3\gamma]\\ &+\cos[A-h_1(\alpha+\beta)-h_2(\alpha-\beta)+h_3\gamma]\\ &+\cos[A+h_1(\alpha-\beta)-h_2(\alpha+\beta)-h_3\gamma]\\ &+\cos[A-h_1(\alpha-\beta)+h_2(\alpha+\beta)-h_3\gamma]\\ =\ &2\{\cos(A+h_3\gamma)\cos[h_1(\alpha+\beta)+h_2(\alpha-\beta)]\\ &+\cos(A-h_3\gamma)\cos[h_1(\alpha-\beta)-h_2(\alpha+\beta)]\},\end{aligned}$$

which after some reduction gives:

$$\begin{aligned}\frac{S}{32O} = &\cos A\cos(h_1\alpha-h_2\beta)\cos(h_2\alpha+h_1\beta)\cos h_3\gamma\\ &+\sin A\sin(h_1\alpha-h_2\beta)\sin(h_2\alpha+h_1\beta)\sin h_3\gamma.\end{aligned}$$

If in this formula we put $\alpha=\beta=\gamma=0$, the points assume the position of the Ca-atoms. Remembering that 4 points join in each Ca-centre, we obtain for the structure-factor of Ca:

$$\frac{S}{8\,.\,Ca} = \cos A.$$

Putting $\alpha=\beta=0$ and $\gamma=\pi$, we obtain the structure factor of the W atoms:

$$\frac{S}{8W} = (-1)^{h_3}\cos A.$$

Dividing by 32O, we finally obtain for the structure factor of the whole lattice:

$$\begin{aligned}\frac{S}{\cos A} = &\frac{Ca+(-1)^{h_3}W}{4O}+\cos(h_1\alpha-h_2\beta)\cos(h_2\alpha+h_1\beta)\cos h_3\gamma\\ &+\mathrm{tg}\,A\,.\,\sin(h_1\alpha-h_2\beta)\sin(h_2\alpha+h_1\beta)\sin h_3\gamma\end{aligned} \quad . \ . \ . \quad (11)$$

Putting Ca = 20, W = 74, O = 8, we obtain :

(1) $\Sigma h = 4n$, $\cos A = \pm 1$, $\sin A = 0$.

$$S = 2{\cdot}938 + \cos(h_1\alpha - h_2\beta)\cos(h_2\alpha + h_1\beta)\cos h_3\gamma.$$

(2) $\Sigma h = 4n+2$, $\cos A = 0$, $\sin A = \pm 1$.

$$S = \sin(h_1\alpha - h_2\beta)\sin(h_2\alpha + h_1\beta)\sin h_3\gamma.$$

(3) $\Sigma h = 4n \pm 1$, $\cos A = \pm\frac{1}{\sqrt{2}}$, $\sin A = \pm\frac{1}{\sqrt{2}}$.

$$S\sqrt{2} = -1{\cdot}688 + \cos(h_1\alpha - h_2\beta)\cos(h_2\alpha + h_1\beta)\cos h_3\gamma + \operatorname{tg} A \sin(h_1\alpha - h_2\beta)\sin(h_2\alpha + h_1\beta)\sin h_3\gamma.$$

The intensities of the lines are then calculated from the formula (3). In calculating these values we must remember that when h_1 and h_2 are unequal $S_{h_1h_2h_3}$ will be different from $S_{h_2h_1h_3}$ and must be calculated separately.

Having to deal with three parameters, an accurate determination merely by means of the intensity calculations is not a very easy matter. After considerable work we found that the values $\alpha = 20°$, $\beta = 20°$, $\gamma = 72°$ give a very satisfactory agreement between observed and calculated intensity distribution.

In the case of powellite the metallic atoms are not so dominating, and therefore the intensities in this case are more sensitive to variation of the parameters of the oxygen atoms. Although the parameters undoubtedly are somewhat different for the two minerals, we have used the same parameter for powellite. The observed and calculated intensities are given in Tables VI. and VII., and are perhaps better seen from figs. 12 and 13.

We notice that the intensity distribution found theoretically is essentially the same as that observed, and we are undoubtedly dealing with the right type of lattice.

The parameter values are probably near to the true ones, but we have not gone further in the very laborious work of improving the values by means of the intensity calculations.

In trying to obtain exact parameter values the difficulties met with are not merely due to the laborious calculation work, but they are partly due to the fact that we do not know exactly the accuracy of our fundamental theoretical formulæ. Thus, if the lattice is built of ions and not of neutral atoms, the scattering power (reflecting power) is not proportional to the atomic number. To the first approximation this might be accounted for if in the case of a negative ion we add to and for positive ions subtract from the atomic number so many units as the ion contains free elementary charges. But even then the formulæ can only give the intensities with a certain approximation.

Fig. 12.

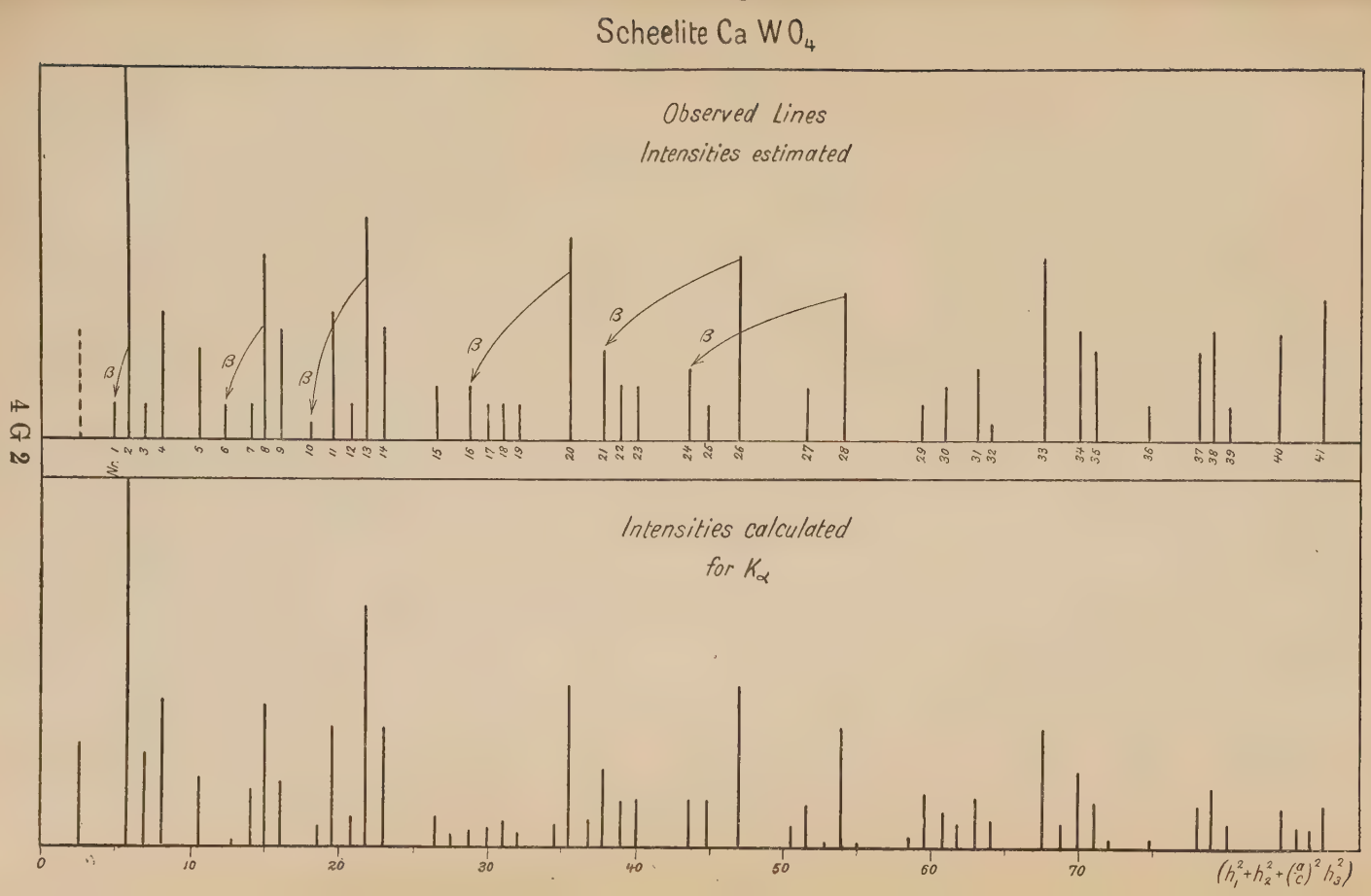
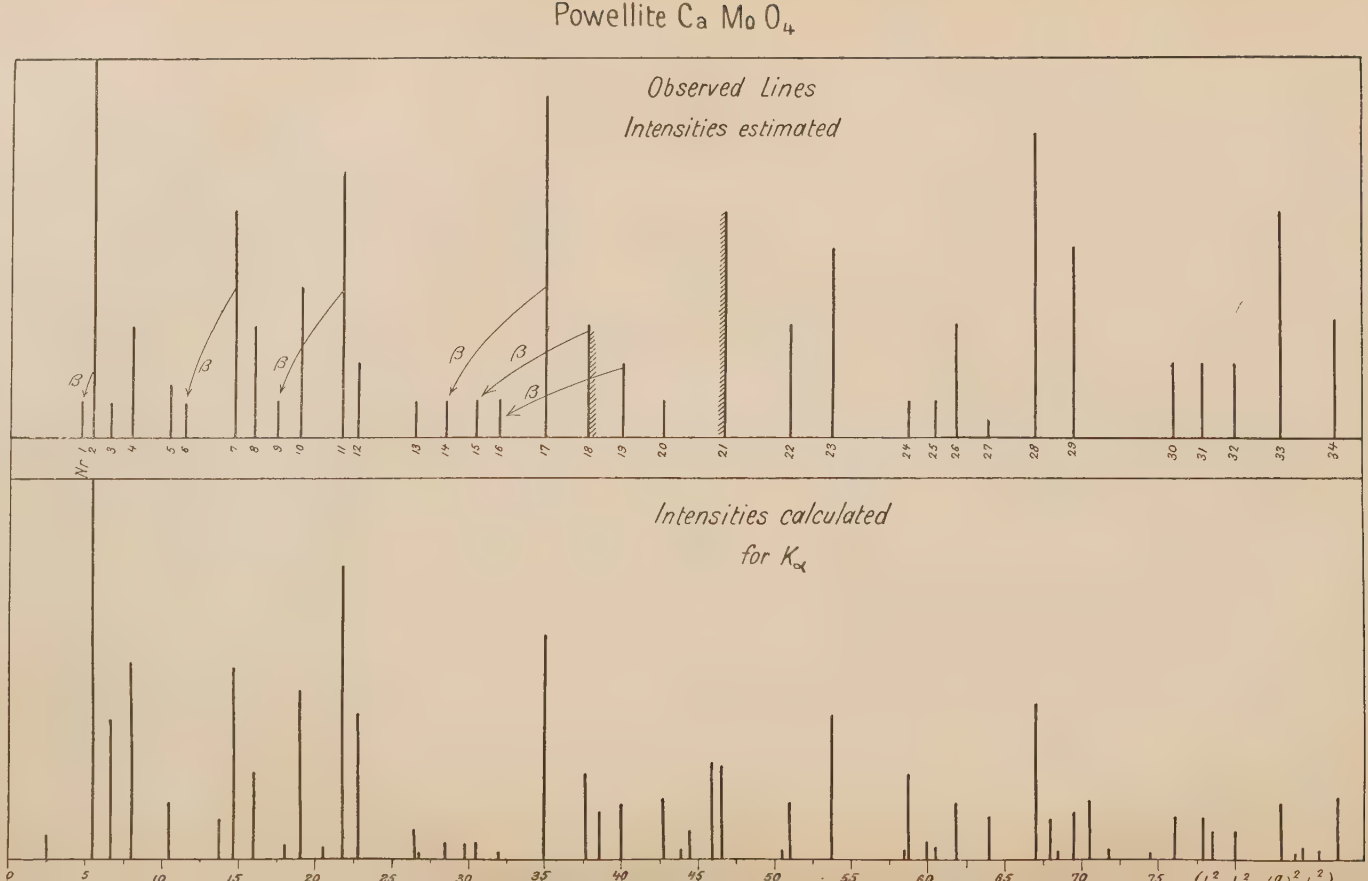

Scheelite Ca W O4
Observed Lines
Intensities estimated
β
Nr. 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
Intensities calculated
for Kα
0
10
20
30
40
50
60
70
$(h_1^2+h_2^2+(\frac{a}{c})^2 h_3^2)$
4 G 2

Fig. 13.


Powellite Ca Mo O_4
Observed Lines
Intensities estimated
β
Nr 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
Intensities calculated
for K_α
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
$(h^2+k^2+(g)^2/c^2)$

Perhaps the most serious incompleteness of the formula results from the fact that the electrons are not united in a space small as compared with the dimensions of the elementary lattice, and according to the distribution of electrons the way in which the intensity varies with ϕ for different sorts of atoms will be different.

We can therefore at present hardly push things further than to obtain a theoretical reproduction of the typical features of the intensity distribution.

In the case of scheelite a number of intensity measurements were made by means of the Bragg ionization method, and as a check we have calculated the intensities by means of our intensity formula.

The result of this comparison is given in Table VIII., and we notice that the agreement is good.

TABLE VIII.

Refl. plane.						
		Indices	4.0.0	8.0.0		
(100)	I	obs.	1	0·3		
		cal.	1	0·44		
		Indices	0.0.4	0.0.8		
(001)	I	obs.	1	0·2		
		cal.	1	0·2		
		Indices	2.2.0	4.4.0	6.6.0	
(110)	I	obs.	1	0·4	0·2	
		cal.	1	0·1	0·1	
		Indices	2.0.2	4.0.4	6.0.6	
(101)	I	obs.	1	0·44	0·22	
		cal.	1	0·36	0·17	
		Indices	1.1.1	2.2.2	3.3.3	4.4.4
(111)	I	obs.	1	0	0·2	0·9
		cal.	1	0	0·1	0·5

Before arriving at this final solution we have tried a considerable number of other possibilities, and we may here mention the following :—

(1) The oxygen atoms are divided in two groups of 16. One group is associated with Ca, one with W, so that the lattice is formed by groups O—M—O, where M is the metal atoms, and where the axis is parallel to the c-axis. The lattice, however, has too high symmetry, and the planes for which $h_3=0$ and h_1h_2 even give a too large intensity relative to other planes.

(2) The oxygen atoms are placed on horizontal lines [100] and [010] through the Ca-atoms. This case is derived from the general formula (11) by putting $\alpha=\beta$ and $\gamma=0$.

The symmetry would be too high, the ratio c/a would be smaller than unity, and the intensity of reflexions like (004) (008) too strong.

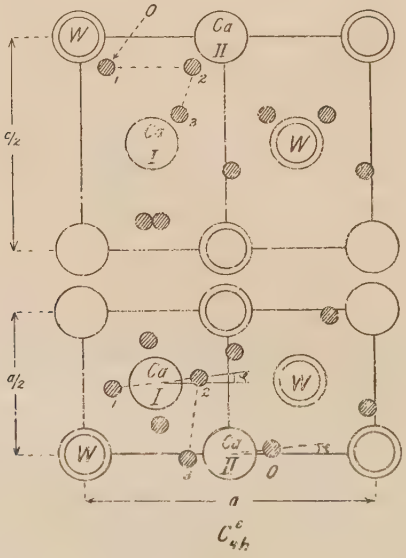
(3) The oxygen atoms are placed on digonal axis [110] and [1–10] through the centres of symmetry. This case is derived from (11) by putting $\alpha=-\pi/4$, $\gamma=-\pi/4$. Symmetry too high, the reflexion from (004) too weak and that of (008) too strong.

(4) The oxygen atoms are situated on the diagonal planes (110) (1–10). This case corresponds to $\beta=0$. Apart from the fact that the symmetry is too high, this arrangement for $\alpha=20°$, $\gamma=70°$ gave a better agreement than the three previous cases. For lines with even indices we obtain a satisfactory intensity distribution, but not for lines with odd indices. Thus the intensity for the plane (311) came out too weak by calculation.

Atomic Dimensions.

§ 10. If we regard the atoms as spheres in contact, the lattice may permit the following contacts:—Each oxygen

Fig. 14.



C_{4h}^{6}

Scheelite-group

atom (2) makes contact with one W atom and 2 Ca atoms (I and II, fig. 14).

If we regard the oxygen atoms to exist as negative ions with a large "radius," the oxygen atoms may be mutually in contact.

One oxygen atom (2) may probably be in contact with two other oxygen atoms (1, 3, fig. 14).

The centre distances are determined by the following formulæ:

$$\left.\begin{aligned}
\mathrm{O-Ca\,(I)} &= a\sqrt{l^2+m^2+\kappa^2n^2}\\
\mathrm{O-Ca\,(II)} &= a\sqrt{(\tfrac{1}{4}-l)^2+(\tfrac{1}{4}+m)^2+\kappa^2(\tfrac{1}{4}-n)^2}\\
\mathrm{O-W} &= a\sqrt{(\tfrac{1}{4}-l)^2+(\tfrac{1}{4}-m)^2+\kappa^2(\tfrac{1}{4}-n)^2}\\
\mathrm{O_1-O_2} &= 2a\sqrt{l^2+m^2}\\
\mathrm{O_2-O_3} &= a\sqrt{(2l-\tfrac{1}{4})^2+(2m+\tfrac{1}{4})^2+\kappa^2(2n-}
\end{aligned}\right\}. \quad (12)$$

where $\kappa=\frac{c}{a}$.

The parameters previously used for the intensity calculations were:

$$l = 0{\cdot}111, \quad m = 0, \quad n = 0{\cdot}2.$$

These values give:

$$\begin{aligned}
\mathrm{O-Ca\,(I)} &= 2{\cdot}415\ \text{Å}.,\\
\mathrm{O-Ca\,(II)} &= 2{\cdot}201\ ,, \quad = \mathrm{O-W},\\
\mathrm{O_1-O_2} &= 1{\cdot}65\ ,,\\
\mathrm{O_2-O_3} &= 2{\cdot}53\ ,,
\end{aligned}$$

As we see, the centre distances between O and Ca and between pairs of oxygen atoms do not come out exactly equal. Now we cannot be sure that they really are equal, but the difference of centre distances is so small that it is possible to make them equal by small modifications of the parameters. The parameters should then fulfil the following conditions:

$$\left.\begin{aligned}
\mathrm{O-Ca\,(I)} &= \mathrm{O-Ca\,(II)},\\
\mathrm{O_1-O_2} &= \mathrm{O_2-O_3}.
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (13)$$

These conditions give two equations between three parameters. To obtain a third condition we assume that the oxygen atoms exist in the form of negative ions, and that the diameter is about the same as found in the case of zircon.

Putting the centre distance $O-O=2\cdot25$, the conditions (13) give for the parameters:

$$l = 0\cdot151, \quad \alpha = 28^{\circ}\cdot4,$$
$$m = 0\cdot007, \quad \beta = 25^{\circ}\cdot9,$$
$$n = 0\cdot170, \quad \gamma = 61^{\circ}\cdot3.$$

These parameters give the following dimensions of the ions of scheelite:

$$\rho_O = 1\cdot125 \text{ Å.},$$
$$\rho_{Ca} = 1\cdot11 \text{ ,,}$$
$$\rho_W = 1\cdot04 \text{ ,,}$$

If we apply the same parameter values to powellite, we obtain:

$$O-Ca\,(I) = O-Ca\,(II) = 2\cdot235,$$
$$O_1-O_2 = O_2-O_3 = 2\cdot235,$$
$$O-Mo = 2\cdot15,$$

and

$$\rho_O = 1\cdot12 \text{ Å.},$$
$$\rho_{Ca} = 1\cdot12 \text{ ,,}$$
$$\rho_{Mo} = 1\cdot03 \text{ ,,}$$

Since these results were obtained, investigations on the structure of other members of the scheelite group have been continued at my laboratory. The structure of $BaWO_4$, $BaMoO_4$, $PbWO_4$, and $PbMoO_4$ has been studied by Mr. Alf Refsum by means of the powder method. He finds that all of them have the same structure as scheelite, and the parameters previously used for scheelite give a good agreement between calculated and observed intensities for the whole group of minerals. Details will be given in a separate paper.

The parameters which we have derived by means of the conditions of contact do not differ much from those used for the intensity calculations. We can therefore take it for granted that these somewhat modified parameters would also give a satisfactory agreement between observed and calculated intensities.

If the parameters finally found are correct, it would mean (as $m \neq 0$) that the oxygen atoms are not placed exactly in the planes (100) and (010) through the Ca-atoms, but in planes forming an angle ϕ with these planes (see fig. 14), where

$$\operatorname{tg}\phi = \frac{m}{l} = 0\cdot0465,$$

$$\phi = 2^{\circ}\,7.$$

When these "contact" conditions are fulfilled, the lattice, regarded as a system of spheres, should be very stable.

Each W-atom is surrounded by 4 O-atoms, whose centres are placed at the corners of a tetrahedron, which is somewhat compressed in the direction of the *c*-axis.

Each Ca-atom is in "contact" with 8 oxygen atoms, and each oxygen atom touches two Ca-atoms, one W-atom, and two other oxygen atoms.

In conclusion I wish to express my sincere thanks to Mr. Egil A. Hylleraas for his most valuable assistance in connexion with this work.

Physical Institute,
University, Oslo.
October 1925.

CV. *The Orientation of the Oxygen Molecule in a Magnetic Field.* *By* L. C. Jackson, *M.Sc.*, *Ph.D.*, *A.Inst.P.*, "1851 *Exhibition*" *Senior Student* *.

ACCORDING to the quantum theory, as developed by Pauli, Sommerfeld, Landé and others, an atom or a molecule possessing a magnetic moment, when placed in a magnetic field, cannot take up any arbitrary orientation with regard to the direction of the field. It can take up only a discrete number of possible orientations determined by certain quantum restrictions. This theory of spacial quantization has been tested and confirmed experimentally by Gerlach and Stern †. Their classical experiments are so well known that any detailed description is unnecessary here. It may merely be mentioned that a very narrow stream of atoms produced by boiling various metals (Ag, Cu, Tl, etc.) is allowed to pass through a very non-homogeneous magnetic field and to fall on a glass plate on which a visible deposit is eventually formed.

The effect of the magnetic field is to split up the stream of atoms into as many separate streams as there are possible quantum orientations for the atom in its particular state. Thus it was predicted and verified that a stream of silver

* Communicated by the Author.

† Stern, *Zeits. für Phys.* vii. p. 249 (1921); Gerlach & Stern, *ibid.* viii. p. 110 (1921); ix. p. 349 (1922); Gerlach & Cilliers, *ibid.* xxvi. p. 106 (1924); Gerlach & Stern, *Ann. der Phys.* lxxiv. p. 673 (1924); Gerlach, *ibid.* lxxvi. p. 163 (1925).

atoms existing in a singlet '*s*' state, corresponding to a magnetic moment equal to one Bohr magneton, would be split up into two streams equally disposed on either side of the zero position. The separation of the streams, which is inversely proportional to the mass of the atom and the square of its velocity, was small in Gerlach and Stern's experiments, of the order of a fraction of a millimetre. The experiments are moreover very difficult. One might therefore consider whether the experiment would be possible with some other material which would give a much larger separation of the component streams. If now a jet of oxygen at atmospheric temperature and at little more than atmospheric pressure were sent through a non-homogeneous magnetic field as in Gerlach and Stern's arrangement, then neglecting for the moment, *merely for purposes of argument*, the effect of the collisions between the molecules on their orientations, one would expect theoretically a very large separation. Thus, taking the velocity in question as that of the jet as a whole, the separation to be expected between the component streams would be of the order of 3 centimetres in place of 0·01 mm.* as in Gerlach and Stern's observations for the same values of the length of path in the magnetic field and of $d\mathrm{H}/dx$. The stream would probably be split up into three separate streams, a central undeviated one and two equidistant ones on either side (2. 0. 2) corresponding to a triplet '*s*' state. Such an experiment could readily be carried out if some means could be found of observing the form of the oxygen stream. How this can be done will be described later.

The proposed experiment differs from that of Gerlach and Stern in two important respects : in the latter, atoms passed through a region of high vacuum while subject to the influence of the magnetic field, so that they passed through without experiencing any collisions, whereas in the other case the oxygen molecules would collide many times while in the magnetic field, and also one would now be dealing with molecules, whereas Gerlach and Stern's observations were carried out, with some possible doubtful exceptions, with atoms. The former difference is of course a fundamental one and the proposed experiment becomes, not one to test the theory of spacial quantization (that can be taken as proved by Gerlach and Stern's experiments), but one to determine the effect of the collisions between the molecules on the orientations taken up by the latter.

* Stern, *Zeits. für Phys.* vii. p. 249 (1921).

The fact that one is now dealing with molecules and not with atoms is an important one, but in the present state of the theory it would be difficult to state definitely whether it really brings in a fundamental difference.

Let us now consider what may be the effect of the collisions in the proposed experiment. One may take it as certain that during a collision the quantum orientations are completely disturbed. If one made the (improbable) assumption that the molecule after the collision returned to the same orientation which it possessed before, one would expect that the oxygen jet would be split up into separate jets but that the separations of the latter would be less than the theoretical value by a factor depending on the ratio of the duration of the collision to the time in the mean free path. Since the time in collision is short compared with that in the mean free path, the effect of the magnetic field should, on this view, be still easily observable.

If, on the other hand, one makes the usually accepted assumption that all the possible quantum orientations are equally probable so that, after collision, the molecule can take up any one of them, one would expect that the experiment would give a null result if the length of path in the magnetic field were large compared with the mean free path. The molecule would then have passed through all the possible quantum orientations provided that a sufficient number of collisions took place in the magnetic field and the resultant component of the magnetic moment of the molecule in the direction of the magnetic field would be zero. It may be pointed out that the equality of the probabilities of the possible quantum orientations though generally accepted is in reality an assumption. The approximate equality in intensity of the deviated lines in Gerlach and Stern's photographs is in agreement with this idea, since it shows that the various quantum orientations are present in equal numbers. Since, however, collisions do not occur in the magnetic field in Gerlach and Stern's arrangement, their experiments do not give any information as to the distribution among the possible orientations when collisions do occur.

If the proposed experiment were to give a null result, it could be interpreted as showing that the assumption of the equality of the probabilities of the various quantum orientations is justified. If, however, a positive result were obtained many factors would have to be considered before the actual meaning of the result could be stated. Oxygen would seem to be a suitable substance for the experiment, since it certainly possesses a magnetic moment and because

the quantities to be observed, apart from the effect of the collisions, are so large.

The experiment now to be described was carried out about two years ago, before the publication of any of Gerlach's later results. The publication of the observation has been unavoidably delayed by various circumstances, and the theoretical side of the question of spacial quantization has advanced notably since the experiment was carried out. It was, however, thought to be of sufficient interest to warrant publication now.

Experimental details.

In a lecture at the Royal Institution * Sir James Dewar showed some very beautiful examples of the use of soap-films as detectors of the forms and movements of gaseous jets. If a jet is allowed to impinge obliquely on a soap-film attached to a circular ring of wire or to the end of a wide tube, a system of two beautifully coloured stationary vortices is produced. If now light from an arc lamp is reflected from the soap-film and allowed to fall on a screen some distance away, an enlarged image of the vortex system can be obtained. The point of impact of the jet on the film and the nearly straight line, dividing the vortices from one another, which shows the direction of the incident jet, both show up well and can be focussed quite sharply. If now a change takes place in the position or the form of the jet, this is immediately obvious through a change in the image of the point of impact and in the vortex system. In the publication quoted above is given a large number of photographs of such vortex systems on soap-films, figs. 25 and 31 showing the effect produced under the conditions of the experiment here described.

Such a soap-film was used by Dewar to demonstrate the paramagnetic properties of oxygen by the deflexion of a jet of the gas in a magnetic field. A jet of oxygen was passed between the conical pole pieces of an electromagnet and allowed to fall on to the soap-film. On switching on the current in the electromagnet, the jet was pulled down into the stronger parts of the field and this was immediately seen by the change in the vortex system. The apparatus used is shown in fig. 46 of the paper † already referred to.

This apparatus, after being modified to suit requirements, was used in the present experiment. The pole pieces were

* Proc. Roy. Inst. xxiv. part 1.

† Dewar, *loc. cit.*

replaced by ones having the same shape as those employed by Gerlach and Stern. Oxygen from a large aspirator arranged to deliver a stream of gas at constant pressure was passed through a fine glass jet suitably arranged with regard to the pole pieces. The stream of oxygen was adjusted as nearly as possible parallel to the edge of the wedge-shaped pole piece. The pressure of the oxygen was so arranged that the velocity of the jet was generally about 15 metres per second. The jet impinged on a soap-film attached to a ring of platinum wire about one inch in diameter placed just outside the field. The image of the film produced on the screen was about three feet in diameter, so that, since a shift of one centimetre of the point of impact of the jet could be readily observed in the enlarged image on the screen, a shift of about 0·3 mm. or rather less of the actual jet could be detected.

The vortex system and the point of impact of the jet on the film were carefully watched as the current was switched on. In *no case was any change in the form of the point of impact observable.* The jet did not, within the limits of fineness of the observations, split up into separate streams nor did it broaden in the direction of $d\mathrm{H}/dx$. The observation was then repeated many times, changing all the variable quantities in succession. Considerable alterations in the velocity of the jet and in the length of path in the magnetic field were made. The current through the electromagnet was increased from a small value up to as much as 15 or 20 amperes for a short time, but in no case was any positive result observed. The actual value of $d\mathrm{H}/dx$ was not measured, but judging by the field strengh obtainable it seemed certain that the largest value of $d\mathrm{H}/dx$ could not have been less than one-tenth of that in Gerlach and Stern's observations. The "theoretical" separation of the component jets for this value of $d\mathrm{H}/dx$ would be easily observable.

This null result is in agreement with the assumption of the equal probability of the possible quantum orientations, and, after considering the various factors which might influence a positive result if such occurred, it may be said that the interpretation of the experiment is probably that the oxygen molecule can after collision take up any one of the possible quantum orientations, passing eventually through them all.

A precise statement of the significance of this result cannot, however, be made until a satisfactory theory has been put forward for the mechanism of the collision of

atoms and molecules in a magnetic field. The result of the experiment described above is now published in the hope of attracting attention to this difficult but important problem.

The experiment was carried out in the Davy-Faraday Laboratory of the Royal Institution, and my thanks are due to the Director, Sir W. H. Bragg, for placing the necessary facilities at my disposal.

The Davy-Faraday Laboratory,
20 Albemarle Street,
London, W. 1.
January 7th, 1926.

CVI. *On the True Signification of Fizeau-Zeeman's Experiments.* *By* Charles L. R. E. Menges *.

THE purpose of the present communication is to discuss the signification of the result obtained in a former paper of the writer †. I have shown that the *usual interpretation* of Fresnel-Fizeau's experiment is essentially erroneous on account of two subtile errors, which depend on each other and which we formerly unconsciously introduced. It seems I have not sufficiently emphasized the importance of my correct interpretation, as it was misunderstood.

The development and signification of Einstein's Relativity Theory is treated by Professsor Dr. J. D. van der Waals, jr., in a very interesting way in two volumes ‡. The first one, issued in 1921, being an introduction to the second one, deals with those points, which, according to the author, lead to Einstein's theory. Fresnel's coefficient and Fizeau's experiment are discussed, obviously with the intention to refer thereto in the second volume in the usual sense as being the decisive experimental confirmation of Einstein's theory. However, in *the second volume the reference expected is not to be found.*

That second volume appeared in 1923. In the meantime, it resulted from my paper on Fresnel's coefficient § that the

* Communicated by the Author.

† "On Kinematics," Phil. Mag. xlix. p. 597 (March 1925).

‡ Dr. J. D. van der Waals, jr., 'Over den Wereldether' (1921); 'De Relativiteits-Theorie' (1923); 'De Erven F. Bohn, Haarlem.

§ *Comptes Rendus*, clxxv. p. 574 (1922).

true interpretation of Fresnel-Fizeau's experiment is essentially different from that formerly generally attributed to it. Professor van der Waals's opinion is obviously that the said experiment can no longer be regarded as decisive between Einstein's theory and the older theories and that it may be left out of consideration now.

Apparently this is also the actual prevailing opinion, for Fizeau's experiment was not even mentioned in last year's extensive discussion on Professor Dayton C. Miller's results obtained on Mount Wilson in repeating Michelson and Morley's so-called æther drift experiment. According to a communication from Professor Einstein to "Science Service"*, he admits now that his theory rests essentially on Michelson and Morley's experiment only, therefore he likewise abandons what he himself repeatedly stated to be the "*experimentum crucis*" or decisive experiment for his theory.

I cannot share that new opinion, as if Fizeau's experiment had no longer any importance in the matter now. The immediate result of Fizeau's experiment is quite certain; in this respect it very much surpasses Michelson and Morley's experiment. This depends on the velocity of the Earth in an hypothetical way; that velocity is a circumstance outside the laboratory, quite beyond our control, not changeable, not reversible. In Fizeau's effect, on the contrary, its main cause and all details are well controllable, exactly determinable, and they may be changed and reversed at will.

Professor Dayton C. Miller claims a result for his repetition of Michelson and Morley's experiment, which is only 30 per cent. at most of the calculated effect. Certainly, Professor Miller observed an effect of the said magnitude, but the question remains: is it due to the alleged æther wind? There is no incertitude of this kind in Fizeau's experiment. This experiment therefore maintains its character as "*experimentum crucis*" (decisive experiment) quite independent of what it proves or disproves, which depends on the *interpretation* of the result.

For more than a century Fresnel's formula and Fizeau's experiment concerning light transmitted by moving substances formed a problem which scientists have tried to solve in different ways. The main point in the problem is the fact that a solution resting on certain well-established

* 'Science,' lxii. Supplement, p. 8 (July 31, 1925).

bases (see below) could not be obtained. Therefore, the generally admitted inferences were :—

1. The solution of the problem on said bases is impossible; to solve the problem any particular hypothesis, suitable to lead to the solution, must be added.

2. The said bases are only approximately, but not essentially, true.

In this sense the last alleged solution is that by means of Einstein's theory, which was originally given by Professor von Laue.

That formerly admitted insight in the question is now wholly null and void in consequence of my solution.

The fact is : *on the said bases, and without introducing any particular hypothesis, I established the formula for the experiment.*

Any formula may be made to fit a particular experiment by means of a suitable chosen so-called constant. However, under different circumstances, it generally will not suit. Only when the formula is correctly based on true general physical laws, will it give with the same constant correct results over a wide range. Especially when the formula proves to be true under the most different circumstances—which is just the case here, as I point out below—then the laws as well as the constant are well confirmed.

To test the validity of physical or other laws, the well-known way is to calculate, according to those laws, the result of experiments and compare it with the actual experimental result. Of course, the calculation must be correct, that is, *all formulæ used must be strictly consistent with the laws to be tested.*

Unconscious deviations from this logical law led to the hitherto encountered difficulties. It is by strictly avoiding such deviation that I arrived at *quite new results*, free from difficulties, free from any old or new doubtful hypothesis.

I emphasize this to avoid my communication being mistaken as analogous with the attempts to refute Einstein's theory, which all mainly aim at reverting to older theories, as, for instance, in Professor E. Gehrcke's controversy with Dr. M. Born *, and in Professor P. Lenard's polemic pamphlets against Einstein's theory.

In the question I here discuss, it is the old idea of a "dragging coefficient" which led to Einstein's theory. *According to my new result the true interpretation of the experiment is radically different to that old idea.* As a

* '*Die Naturwissenchaften*,' i. pp. 62, 92, 170, 191, 338.

consequence then, it follows that Einstein's theory cannot be maintained.

In the same way I treat electromagnetic theory in my books 'Nouvelles vues Faraday-Maxwelliennes' and its 'Supplément—Sur la Propagation de la Lumière' (Gauthier-Villars & Cie, Paris, 1924). I refer thereto concerning the connexion of the actual subject with electromagnetic theory.

I established my formula for the experiment on light transmitted by moving substances, namely for the actual observable shift of the interference fringes, on the following bases :—

1. The laws of Kinematics. For the case in question the result of the velocity v and another velocity $\mp w$ in the same direction is the velocity

$$u = v \mp w.$$

2. The aforesaid laws are generally true, without any exception ; they hold also when one of the velocities, say v is c = the velocity of light in vacuo ; the velocity obtained by compounding c with $\mp w$ is

$$c' = c \mp w.$$

3. The refractive index of a substance is the ratio of the velocity of light outside the substance to the velocity of light inside that substance, both velocities calculated relatively to the substance, according to 1 and 2.

The formula I established on said bases (see my Phil. Mag. paper, and, for further details, my books above referred to) is confirmed by Professor P. Zeeman's experiments *. I particularly mention Zeeman's experiments, as his results are undoubtedly the most accurate so far obtained. *They confirm my equation practically to* 100 per cent. Moreover, his experiments do not only concern moving water, as in former experiments, but also quartz and moving glass. The experimental results with such different substances being in so close accordance with my formula, *they form the decisive confirmation of the fundamentals, as stated under* 1, 2, *and* 3.

The validity of 1 *is the immediate disproof of the formula for compounding velocities in Einstein's theory.*

The validity of 2 *is the immediate disproof of what Einstein's theory admits as its basis.*

* P. Zeeman, *Verslagen Akadem. Amsterdam,* xxi. p. 245 (1914); xxiv. p. 18 (1915); xxvii. p. 1453 (1919); xxviii. p. 1462 (1919); xxix. p. 1252 (1920).

CVII. *The Scattering Powers of Calcium and Fluorine for X-Rays.* *By* R. W. James, *M.A., Senior Lecturer in Physics, Manchester University, and* J. T. Randall, *B.Sc.**

1. *Introduction.*

In determining the arrangement of the atoms in a crystal structure from a consideration of the intensities of the X-ray spectra reflected from the different sets of atomic planes, it is necessary to make allowance for the relative diffracting powers of the various atoms. In many cases it has been sufficient to ascribe to each atom a diffracting weight proportional to its atomic number, and to the number of electrons contained in it. This, however, can only be approximately correct, for the scattering power of an atom must be a function of the angle of scattering. The electrons which contribute to the scattered beam are distributed, in each atom, through a volume whose dimensions are of the same order of magnitude as the distance between the atomic planes and the wave-length of the X-rays used in the investigation. Thus the contributions of the different electrons, in any direction, to the scattered beam will differ in phase, and the phase-difference will depend on the angle of scattering. We may, in fact, write the scattering power of the atom as F, where

$$\mathrm{F} = \mathrm{Z}f(2\theta, \lambda).$$

Z in this expression is the number of electrons contained in the atom or ion; $f(2\theta, \lambda)$ is a function of the angle of scattering 2θ and of the wave-length λ of the rays used, which will approach unity for small values of θ and will, in general, decrease as θ increases. The quantity F will depend, therefore, not only on the total number of electrons in the atom, but on their arrangement, and on the angle of scattering. If we consider, for example, two ions both containing the same number of electrons, but one having a considerably greater nuclear charge than the other, so that its electrons are pulled in much more closely, the value of F for the two ions will be nearly the same at small angles of scattering, but will fall off much more slowly as θ increases for the compact ion than for the more loosely-bound one. Thus the ratio of the diffracting powers of the ions will not remain constant as the order of the spectra increases, and

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

structure-amplitudes calculated on the assumption that it does so will be incorrect.

In determining the simpler structures, where a large amount of information can be obtained from symmetry, and where there are only one or two kinds of atom present, this is of little importance. It becomes highly important, however, in the more complex inorganic crystals, where most of the information has to be derived from consideration of intensities, and where three or four different kinds of atom may be present. For progress in determining these structures it is of the first importance to get some idea of the value of the factor F for as many atoms as possible. The importance of the factor F was first pointed out by Darwin *, and by Compton †, in theoretical papers on the intensity of reflexion of X-rays. An experimental study of the F factor for Na and Cl has been made by W. L. Bragg, James, and Bosanquet ‡, and the value of F for a number of ions has been calculated by Hartree § assuming the forms of the electronic orbits calculated by him from spectral terms. Hartree's F values, with certain modifications, were used by James and Wood ‖ in determining the structure of barium sulphate, and in this crystal in particular it was assumed that the diffracting power of the loosely-built oxygen ion, with its small nuclear charge, would fall away relatively far more rapidly as the angle of scattering increases than that of the compact Ba atom with its nuclear charge of 58. Some assumption of this kind appeared to be necessary to explain the observed spectra at all.

2. *The relative Scattering Powers of Potassium and Chlorine.*

The values of F, both experimental and calculated, depend, however, on the application of certain formulæ whose theoretical basis is not entirely secure, and it would evidently be interesting to obtain direct experimental proof that the relative diffracting powers of two ions or atoms do change with the angle of scattering in the sense assumed. Suppose we have a crystal containing two different ions, each having the same number of electrons, and that in certain spectra the contributions from two ions are always

* Phil. Mag. xxvii. p. 315 (1914).
† Phys. Rev. ser. 2, ix. p. 29 (1917).
‡ Phil. Mag. xlii. p. 1 (1921); xliv. p. 433 (1922).
§ Phil. Mag. l. p. 289 (1925).
‖ Proc. Roy. Soc. A. 109, p. 598 (1925).

exactly out of phase. The amplitudes of the spectra will then be proportional to the difference of the F's for the two ions. If the F's are exactly equal and opposite for some angles of scattering, they ought not to be so for other, higher, angles of scattering. Thus by examining spectra of this type we can test the assumption directly without using any doubtful theories.

Sylvine, KCl, appears to be a suitable crystal of this type. It has the rock-salt structure and contains the ions K^+, Cl^-, each of which has 18 electrons. All the spectra in the crystal having 3 odd indices have structure-amplitudes of the type (K − Cl); thus by observing such spectra at a variety of glancing angles it ought to be possible to see whether the scattering powers are equal at all angles. As a matter of fact, the crystal is not a very suitable one. The nuclear charges are 19 and 17, so that the scales of the electronic orbits will not differ greatly. The intensities of the spectra will be proportional to $\left(\frac{F_K - F_{Cl}}{F_K + F_{Cl}}\right)^2$, or nearly so, since the crystal approaches the mosaic type, and will therefore always be very small, since F_K and F_{Cl} will not differ very much at any angle. As a matter of fact, a careful search failed to reveal any spectra of the type (K − Cl). It must be remembered, however, that we should not expect much difference between the two F's except at high angles of scattering, when even the normal spectra are weak, so that a difference of the amount to be expected theoretically might well have escaped detection with the X-ray intensity at our command. To get definite results, we require two ions whose F's are likely to differ more than those of K and Cl, and, for this reason, a study of the spectra of fluorite, CaF_2, has been made.

3. *Discussion of the case of Fluorite.*

The structure of fluorite was determined by W. L. Bragg *. The calcium atoms lie on a face-centred cubic lattice. If the face-centred unit cube be divided into eight smaller equal cubes, the fluorine atoms lie at the centres of each of these. The structure-amplitude S_{hkl} for the spectrum (hkl) is given by

$$S_{hkl} = \mathrm{Ca}\cos\frac{h+k}{2}\pi\cos\frac{k+l}{2}\pi\cos\frac{l+h}{2}\pi + 2\mathrm{F}\cos\frac{h\pi}{2}\cos\frac{k\pi}{2}\cos\frac{l\pi}{2},$$

* Proc. Roy. Soc. A, lxxxix. p 474 (1914).

where Ca and F are the scattering power of Ca and F in the direction of the spectrum concerned. They are, in fact, the F's for Ca and F, but are written in this way for convenience. There are thus only four types of structure-amplitude :—

(*a*) For all spectra with one odd and two even, or one even and two odd indices, S = 0.

(*b*) For all spectra with three odd indices, S = Ca.

There remain spectra for which all the indices are even, say (2*m*, 2*n*, 2*p*) ; for these we have

(*c*) If *m*, *n*, *p* are all even, or if two are odd and one is even, S = Ca + 2F ;

(*d*) If *m*, *n*, *p* are all odd, or if two are even and one is odd, S = Ca − 2F.

The interesting spectra are those of the type S = Ca − 2F. Assuming the calcium and fluorine to be ionized, Ca^{+2} will contain 18 electrons, and F^-, 10 electrons. Thus, for small angles of scattering, S = Ca − 2F = 18 − 20, and the intensity of the spectrum should be a fraction $\left(\frac{20-18}{20+18}\right)^2 = \frac{1}{361}$ of the normal spectrum of type Ca + 2F at the same angle. It should thus be very small, and, indeed, hardly to be detected with the means at our disposal. But the greater nuclear charge of the calcium may be expected to hold the electron structure far more tightly than the smaller charge of the fluorine. In fact, there is reason to believe that the whole structure of 18 electrons lies within a sphere of diameter about 2·1 Å. in the case of calcium, while the 10 electrons of fluorine probably require a sphere of 2·7 Å. diameter to contain them completely. Moreover, we shall expect a much greater concentration of electrons near the centre in the case of Ca. Hartree's figures indicate, in fact, that whereas, for MoK_α radiation, F for Ca^{+2} will be still about 12, for a scattering angle of 60°, that for F^- will have sunk below 1. Thus at this angle the value of $\left(\frac{Ca-2F}{Ca+2F}\right)^2$ will be $\left(\frac{5}{7}\right)^2$, and, thus, spectra found at angles as large as this should be quite strong relatively to the normal.

It was shown by Pealing * that, while the (200) spectrum † from CaF_2 was extremely weak, the (600) was much stronger, but no examination of other spectra of the type Ca − 2F was

* Proc. Phys. Soc. Lond. xxxiii. p. 297 (1921).

† These spectra are called (100) and (300) in Pealing's paper. We have referred them to the true unit spacing, 5·47 Å., in which case they become (200) and (600).

made. These results were discussed by Yamada *, who ascribed them to the correct cause, but based on these two isolated observations rather more than they can carry. In a paper read before the American Physical Society, of which, however, so far as we are aware, only an abstract has appeared, McInnes and Shedlovsky † described some measurements of the intensities of the various spectra from fluorite. They obtained spectra of the type Ca + 2F, Ca, Ca − 2F, but they do not seem to have considered these results from the point of view of the present paper.

4. *Experimental Results with Fluorite.*

We have made a series of observations of the absolute intensity of reflexion for a number of different spectra from fluorite. In Table I. the results of the observations are summarized. Two different crystals, indicated by (1) and (2), were used. All the faces were ground with emery-paper, which has the effect in most cases of increasing the intensity of reflexion. The intensities ρ are the "integrated reflexions" obtained in the usual manner by rotating the crystal with uniform angular velocity through the reflecting position, and observing the total ionization received by the chamber, correction being made for general radiation. ρ is expressed in absolute measure ‡. The radiation employed was Molybdenum K_α of wave-length $\lambda = 0{\cdot}710$ Å.

The crystals (1) and (2) were both similar in appearance, and showed a considerable amount of blue fluorescence, and the spectra obtained from them are comparable in intensity. In addition, a number of observations were made from a third crystal (3), which was clear and colourless, and appeared to be considerably more warped than the others. The strong spectra from (3) were from 45 to 50 per cent. more intense than the corresponding ones from (1) and (2), and even the weak ones were much stronger. This seems to show that fluorite is some way from being a true mosaic crystal, and that extinction is playing a considerable part in reducing the intensities of the strong spectra. We shall return to this point later.

* Nagaoka Anniversary Volume, p. 121.

† Phys. Rev. ser. 2, xxiii. p. 290 (1924).—(Note added April 22, 1926.) While this paper has been in the press McInnes and Shedlovsky have published this work in much greater detail (Phys. Rev. ser. 2, Feb. 1926, p. 130).

‡ The spectra were all compared directly with the (400) reflexion of NaCl. The absolute intensity of the spectrum for Mo $K\alpha$ was taken as $9{\cdot}4 \times 10^{-5}$. This number is based on the measurements of Wasastjerna.

TABLE I.

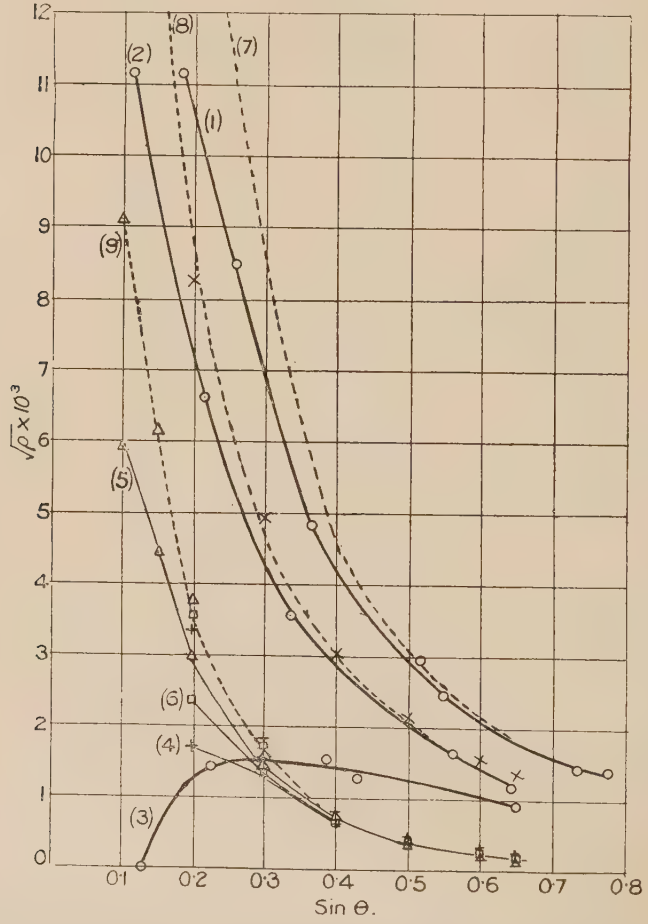
Spectrum.	S.	sin θ.	Crystal.	$\rho \times 10^6$.	$\sqrt{\rho} \times 10^3$.
(111)	Ca	·1124	(1)	124·8	11·18
(113)	„	·2153	(2)	43·7	6·63
(333)	„	·3372	(1)	12·65	3·56
(555)	„	·5620	(1)	2·75	1·67
(339)	„	·6459	(2)	1·45	1·18
(220)	Ca+2F	·1835	(2)	125·0	11·18
(400)	„	·2596	(1)	73·9	8·49
(440)	„	·3670	(2)	23·2	4·82
(800)	„	·5192	(1)	8·72	2·96
(660)	„	·5505	(2)	6·1	2·47
(880)	„	·7340	(2)	2·02	1·43
(1200)	„	·7788	(1)	2·02	1·43
(200)	Ca−2F	·1298	(1)	—	—
(222)	„	·2248	(1)	2·03	1·43
(600)	„	·3894	(1)	2·43	1·56
(226)	„	·4306	(2)	1·62	1·28
(1000)	„	·6490	(1)	0·81	0·90

5. *Discussion of Results.*

The figures in column 6 of Table I., giving the square roots of the intensities, are plotted against the sines of the corresponding glancing angles in fig. 1. It will be seen that the points are grouped on three curves, (1), (2), and (3), corresponding to structure-amplitudes Ca + 2F, Ca, and Ca − 2F respectively. The curve for Ca − 2F is very interesting. No definite (200) spectrum could be observed; at the angle of scattering for this spectrum, 14° 54′, the effect of two fluorine ions almost exactly neutralizes that of the calcium ion. The (222) spectrum, on the other hand, at an angle of scattering of 26° 0′ is quite appreciable, so that the balance is destroyed at this angle, and (600), (226), (10,00) all appear, the latter at an angle of scattering of 80° 56′ being only a little weaker than the (222). Had the ratio of the scattering powers of Ca^{+2} and F^- remained constant as the angle of scattering increased, the spectrum (10,00) would have had an intensity of not more than one per cent. of that of the (200). It is quite evident that, for the higher angles of scattering, either the effect of two

fluorine ions is much less than that of one calcium ion, or that of one calcium ion is much less than that of two fluorine ions. Taking the three curves together, it is evident that the former alternative is the correct one. The three curves

Fig. 1.



To avoid confusion the separate curves for fluorine are not drawn for the higher angles. Corresponding points on the corrected and uncorrected fluorine curves are indicated by the same symbol. Circles are observed points.

differ widely for small angles of scattering, but converge for the larger ones, so that the intensities for angles of about 35° to 40° are of much the same magnitude whether the

structure factor is Ca+2F, Ca, or Ca−2F. The only way in which the results can be explained is by supposing that the F factor for fluorine becomes less and less in comparison with that for calcium as the angle of scattering increases, so that, at large angles, it matters comparatively little whether the effect of the fluorine is added to or subtracted from that of calcium or not. The curves seem to prove, in fact, in a very direct way, apart from any assumptions, that the scattering power of fluorine becomes small at large angles of scattering.

6. *Calculation of Intensity due to Fluorine alone.*

Although there is no spectrum for which the structure-amplitude is due to fluorine alone, it is possible to calculate its effect by combining the other curves. If the crystal were of the ideal mosaic type for which the intensities of the spectra are proportional to the squares of the structure-amplitudes, the square roots of the intensities should be proportional to the amplitudes scattered by the atoms. The difference of the ordinates of curves (1) and (2) divided by two should therefore give the ordinates of the curve on which the intensities of the spectra due to fluorine alone, if such existed, would lie. We could also obtain this curve by subtracting the curve for Ca−2F from that for Ca, and also by subtracting Ca−2F from Ca+2F, and the curves obtained in these three ways should agree. Curves (4), (5), and (6) show the fluorine curves obtained in these three ways in the order stated. It will be seen that, while they agree very well for large angles, they are widely divergent for the smaller ones.

The additive law thus breaks * down, but the manner in which it does so suggests that the crystals used were too perfect to be treated as an ideal mosaic. The strong spectra will thus be much reduced by extinction, or, in other words, the effective absorption coefficient at the reflecting angle will depend on the intensity of the spectum. The curve (4) was obtained from Ca+2F and Ca, for both of which the spectra are strong at small angles, while for each of the other two curves the Ca−2F curve was used, for which the increased absorption due to extinction is nearly negligible; and if the extinction is at all strong, we should also expect the difference to be much less for the large angles, since the weaker high-order spectra are but little affected by extinction.

* This result was also noticed by McInnes and Shedlovsky.

7. *Allowance for Extinction.*

We have tested this idea by trying to make some allowance for extinction. It was shown in the case of rock-salt *, for which the extinction is probably mainly secondary †, that the effective absorption coefficient for a spectrum of intentensity ρ was $\mu_0+\alpha\rho$, where μ_0 is the ordinary absorption coefficient when the crystal is not reflecting and α is almost constant. Suppose that the extinction in the case of fluorite is of this type. On the assumption that the crystal is an ideal mosaic, the integrated reflexion ρ for a spectrum, occurring at a glancing angle θ, and for which the sum of the F factors for the atoms in one molecule is ΣF ‡, is given by

$$\rho=\frac{N^2\lambda^3}{4\mu}\cdot\frac{e^4}{m^2c^4}(\Sigma F)^2\cdot\frac{1+\cos^2 2\theta}{\sin 2\theta}\cdot e^{-BT\sin 2\theta}. \quad . \quad (1)$$

In this formula, N is the number of molecules per cubic centimetre, λ the wave-length of the radiation employed, and μ the linear absorption coefficient.

The exponential term makes allowance for the heat-motions of the atoms, while e, m, and c have the usual significance. We have assumed that μ is to be replaced by $\mu_0+\alpha\rho$, where μ_0 is the ordinary absorption coefficient when the crystal is not reflecting, and have made an estimate of α.

For this purpose the (111) spectrum was used. This occurs at a small angle, is strong, and is due to Ca alone. The temperature factor, which is not known for this crystal, will in any case be small at this angle and is neglected. There is some uncertainty about F. But whatever assumption is made about the distribution of the electrons in the Ca^{+2} ion, the value of F_{Ca} must approach 18 for $\theta=0$, and hence, for a small angle of scattering, such as that for (111), we shall probably not make a large error if we assume Hartree's value for Ca^{+2}. The value of F for $\sin\theta=\cdot1124$ is 15·5, and we have used this in the calculation. The value of μ_0 as measured, using a thin slip of fluorite, is 31·3.

* Phil. Mag. xlii. p. 1 (1921).

† Darwin, Phil. Mag. xliii. p. 800 (1922).

‡ It is assumed throughout that the "average atoms" are spherically symmetrical, so that F depends only on θ and not on the particular direction of the scattered beam with reference to the crystal axes. This no doubt is only approximately correct for more complicated crystals, but appears to be very nearly the case in simple ionized structures.

The calculated value of ρ for (111), using this value of μ_0, came out to be $284{\cdot}5\times10^{-6}$, whereas the observed value is $124{\cdot}8\times10^{-6}$. Assuming that the difference is due to extinction, we have

$$\frac{\mu_0+\alpha\rho}{\mu_0}=\frac{284{\cdot}5}{124{\cdot}8}=2{\cdot}28,$$

whence, putting $\mu_0=31{\cdot}3$, $\rho=124{\cdot}8\times10^{-6}$, we obtain

$$\alpha=3{\cdot}21\times10^{5}.$$

We may call α the "extinction coefficient." If μ is the effective absorption coefficient for a spectrum of intensity ρ, we may write

$$\mu=\mu_0+\epsilon \quad \text{where} \quad \epsilon=\alpha\rho.$$

For (111), $\epsilon=40{\cdot}3$, $\mu=71{\cdot}6$, so that the effective absorption coefficient is more than twice the normal one. For the weak (800), $\epsilon=2{\cdot}8$ and $\mu=34{\cdot}1$; thus the intensity is very little affected by extinction.

Having obtained this value of the extinction coefficient α, we can now correct the observed curves by multiplying the ordinates by the corresponding values of $\sqrt{\frac{\mu_0+\epsilon}{\mu_0}}$. In this way, the corrected curves (7) and (8) in fig. 1 were obtained for Ca + 2F and Ca; the corrected curve for Ca − 2F is not distinguishable for the uncorrected one on the scale of the diagram.

From these corrected curves the three fluorine curves were recalculated. These are shown in curves (9) in fig. 1, and it will be seen that the discrepancies for small angles of scattering have nearly disappeared, while the agreement remains good for the larger angles. The crosses in fig. 1 represent the points obtained for Ca from the curves Ca − 2F and Ca + 2F, which are given for comparison with the corrected Ca curve.

Thus the corrected observations are consistent with one another, and support the assumption that the extinction in fluorite is largely secondary *; that is to say, that the

* It must be emphasized that the values of the extinction determined in this way are valid only for the particular crystal used. Fluorite is certainly very variable in its degree of perfection. The high values of ρ from crystal (3) have already been mentioned. At the other extreme, a particularly clear cleavage fragment gave a value $\rho=47\times10^{-6}$ for (111). After grinding with emery, the same face gave $\rho=113\times10^{-6}$.

homogeneous fragments of the crystal mosaic are not large enough to reflect totally the radiation falling on them. There may, however, be some primary extinction, for some of the weak spectra obtained from crystal (3) were stronger than the corresponding ones from (1) and (2), even when the latter have been corrected. It must be remembered, however, that spectra for which the absolute intensity is 2×10^{-6} or less are very difficult to measure accurately, and that very considerable percentage errors in these are possible.

In Table II. we give the values of ρ for the smoothed observed curves for a series of values of $\sin\theta$, together with the corresponding corrected values.

TABLE II.

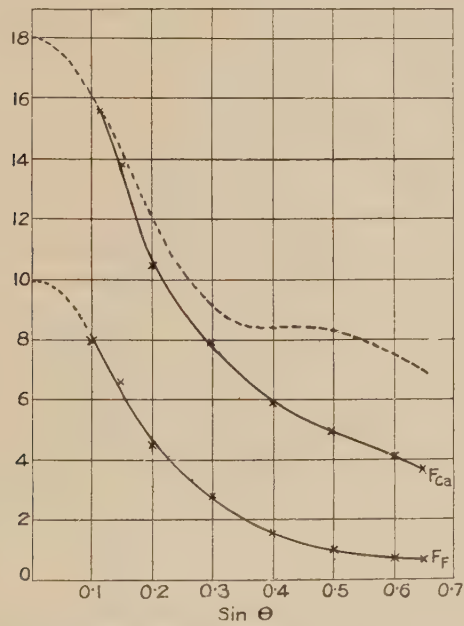
Sin θ		0·1	0·15	0·2	0·3	0·4	0·5	0·6	0·65
Ca+2F	$\rho \times 10^6$	—	—	10·59	6·89	4·19	2·96	2·11	1·77
	ρ corr.	—	—	15·52	8·41	4·65	3·07	2·16	1·80
Ca	ρ	11·73	9·33	7·11	4·29	2·89	2·05	1·45	1·23
	ρ corr.	18·23	12·84	8·76	4·69	3·01	2·09	1·46	1·24
Calculated from Ca+2F and Ca−2F		—	—	8·39	4·96	3·05	2·16	1·	1·36
Ca−2F	ρ	—	0·59	1·26	1·50	1·45	1·24	1·03	0·92
	ρ corr.	—	0·59	1·27	1·52	1·46	1·25	1·04	0·92
$\frac{1}{2}\{(Ca+2F)-Ca\}$ F	ρ	—	—	1·74	1·30	0·65	0·46	0·33	0·27
	ρ corr.	—	—	3·38	1·86	0·82	0·49	0·35	0·28
$\frac{1}{4}\{(Ca+2F)-(Ca-2F)\}$	ρ	—	—	2·33	1·35	0·68	0·43	0·27	0·21
	ρ corr.	—	—	3·56	1·72	0·80	0·45	0·28	0·22
$\frac{1}{2}\{Ca-(Ca-2F)\}$	ρ	5·86	4·37	2·92	1·39	0·72	0·40	0·21	0·16
	ρ corr.	9·11	6·12	3·74	1·58	0·78	0·42	0·21	0·16

8. *The* F *Curves for Calcium and Fluorine.*

In fig. 2 the F curves for calcium and fluorine are plotted against the sines of the glancing angles. These curves were obtained by substitutiug in formula (1) of section 7. The

values of ρ were obtained from the corrected curves for Ca and F; in the case of fluorine, where the curve was obtained in three ways, a mean curve was drawn. The curves are uncorrected for the temperature factor, the value of which is not known for fluorite. Allowance for this factor would make little difference to the curves for small values of θ, but would considerably increase the values of F for the larger angles. Hartree's curve for Ca^{+2} is given for comparison.

Fig. 2.



The dotted curve is Hartree's curve for Ca^{+2}.

It must, of course, be remembered that the curve for Ca is forced to fit Hartree's curve at small angles by the method of correction. The Ca curve falls away much more rapidly than Hartree's curve for moderate angles, and it is unlikely that the temperature factor will account for all the difference. Possibly the cause of the discrepancy is to be sought in the increasing fraction of the incident radiation which at high angles of scattering will undergo Compton scattering, and will therefore probably not take part in the interference.

The calculated values of F uncorrected for temperature factor are given in Table III.

TABLE III.

Sin. θ	0·1	0·15	0·2	0·3	0·3	0·5	0·6	0·65
Ca^{+2}.....	15·8	13·8	10·5	7·9	5·9	4·9	4·1	3·6
F^-	7·9	6·6	4·5	2·8	1·5	1·0	0·70	0·60

9. *Summary.*

(1) The absolute intensities of reflexion have been measured for a series of spectra from fluorite. The structure-amplitudes in the crystal are of three types Ca + 2F, Ca, and Ca − 2F, and the observed spectra are grouped on three corresponding curves.

(2) The spectra of type Ca − 2F are absent or very small for small glancing angles, but become much more important relatively to those of type Ca and Ca + 2F at larger glancing angles. This shows in a direct way that the value of the scattering power F for fluorine becomes less and less important relatively to that for calcium at large angles of scattering.

(3) Curves showing the variation of the square root of the integrated reflexions for the three types of spectra are given. From these curves it is possible to calculate the curve for fluorine in three different ways. The curves so obtained are divergent for small glancing angles, but agree at higher ones. The divergence is ascribed to increased absorption due to "extinction." On the assumption that the extinction is proportional to the observed intensity, a correction is applied which removes most of the difference between the three curves.

(4) The F curves for fluorine and calcium are obtained from the observations, and are compared with those calculated by Hartree.

We wish in conclusion to express our thanks to Prof. W. L. Bragg, F.R.S., for his interest and advice during the course of this work. Part of the apparatus used was purchased by means of a grant from Messrs. Brunner, Mond, Ltd., to whom our thanks are also due.

Manchester University,
Feb. 8, 1926.

CVIII. *Notices respecting New Books.*

Higher Mathematics for Students of Engineering and Science. By F. W. G. Brown. (Macmillan & Co., 1926. 10*s*.)

IN writing this book the author has had particularly in mind the needs of Engineering Students, and his object has been to deal in a single volume with all the branches of pure mathematics required for an engineering degree. The amount of Calculus and Analytical Geometry given is, however, rather greater than that required by the engineering syllabuses in most universities. The general style of the book is good, and it should prove a welcome addition to the rapidly increasing number of introductory treatises addressed not to the mathematical student, but to those who are concerned only with the applications of mathematics to problems in the various branches of science and industry.

Vectorial Mechanics. By L. Silberstein, Ph.D. Second Edition. (Macmillan & Co., 1926. 10*s*.)

This new edition of Dr. Silberstein's important and valuable work, first issued in 1913, differs from the original edition by the inclusion of some Miscellaneous Notes. The first is concerned with a projective or non-metrical generalization of the concept of vector equality. Another contains a concise exposition of the theory of linear vector operators, and the last gives a simplified vectorial deduction of the properties of Euler's angles determining the orientation of a rigid frame.

These new notes add to the usefulness of the volume. The book gives a short but essentially complete exposition of mechanics, and it should also be of value as an introduction to the algebra and analysis of vectors.

The Theory of Functions of a Real Variable and the Theory of Fourier's Series. By E. W. Hobson. Second Edition, revised throughout and enlarged. Vol. 2. (Cambridge University Press, 1926. 50*s*. net.)

Professor Hobson's volume of the Theory of Functions of a Real Variable, which was originally issued in 1907, has now been reissued in two volumes, the first in 1921 and the second in 1926. Almost the whole of the matter presented in the present volume has been rewritten, and a great deal of new material has been added, material based on the investigations of a number of mathematicians in the intervening period. Thus considerable space has been allotted to a discussion of various theories of integration due to Young, Tonelli, and Perron; a full discussion is given of the theories of conventional summation due to Cèsaro, Hölder, and Marcel Riesz; F. Riesz's classification of summable functions is also included. A special feature of the volume is the prominence given to the General Convergence Theorem, which is

treated very fully. On this discussion depends the treatment of the convergence of Fourier's series and Integrals given in later chapters. There is also an account of the interesting modern theory of Fourier transforms.

Matrices and Determinoids. Vol. 3, Part 1. By C. E. Cullis. (Cambridge University Press, 1925. 63*s.* net.)

The volume under review gives a further large instalment of Professor Cullis's large work. The printing of volume 3 was suspended for several years during the completion of some investigations which have necessitated the division of it into two parts and the carrying forward of some of the matter designed for it into a later volume.

The present book is a mine of information, and, like the previous volumes, should be of the greatest value to those working on the subjects with which it deals.

An Introduction to the Theory of Infinite Series. By T. J. I'A. Bromwich. Second Edition revised with the assistance of T. M. MacRobert. (London: Macmillan & Co., 1926. 30*s.* net.)

It is a great satisfaction to welcome the second edition of Dr. Bromwich's 'Infinite Series.' The first edition was issued in 1908, and during the last few years copies have been very difficult to obtain. In the new edition Dr. MacRobert has rendered valuable assistance to the author.

There are various minor changes in the new edition. A discussion of the solution of linear differential equations of the second order has been added; also an account of certain elliptic function formulæ. In the chapters concerned with asymptotic expansions an exposition of the asymptotic expansions of Bessel functions is now included.

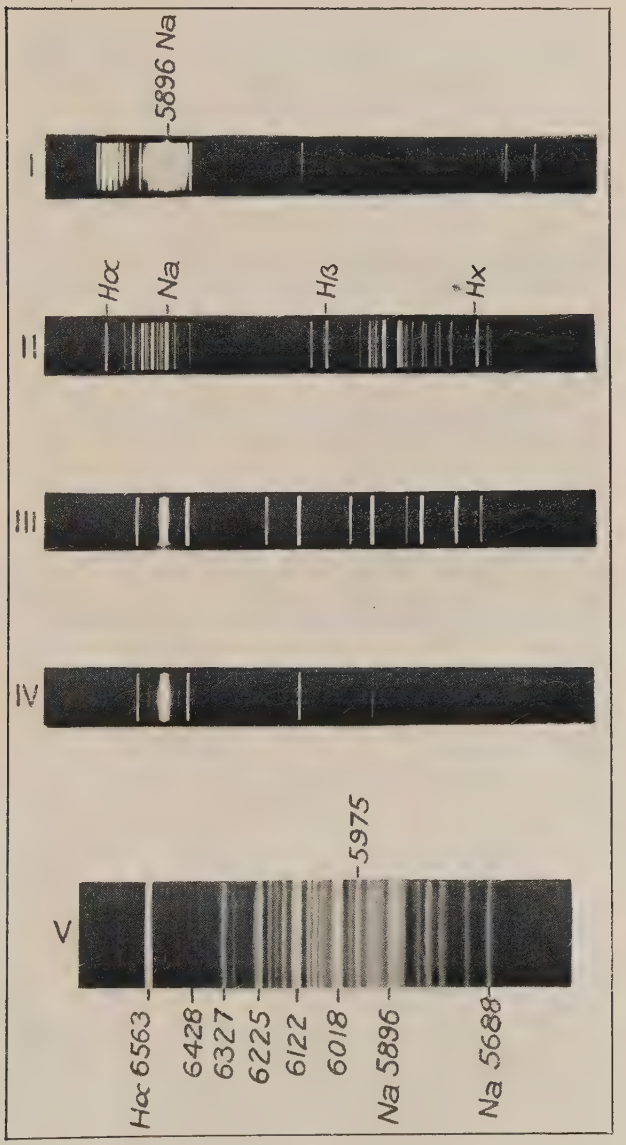
To the appendices there is added an account of Napier's invention of logarithms.

Principles of Geometry. Vol. IV. *Higher Geometry.* By H. F. Baker. (Cambridge University Press, 1925. 15*s.* net.)

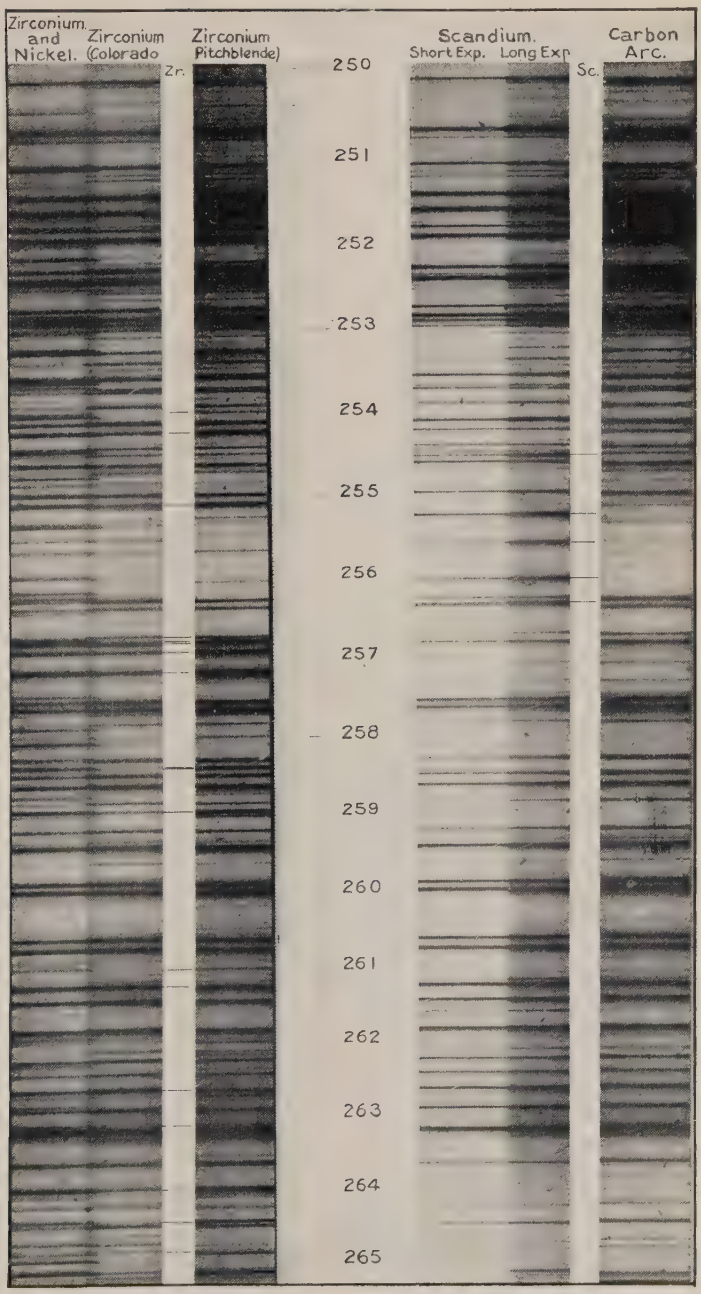
This volume of Professor Baker's 'Geometry' is concerned with showing the utility of the consideration of higher space, especially of four and five dimensions. It is a remarkable fact that it is possible to comprehend under one simple point of view the introduction to nearly all the surfaces ordinarily studied in the geometry of three dimensions, as well as the usual line geometry. The present volume develops this point of view.

The student of geometry will give the present volume the same warm welcome which has been extended to the volumes previously issued. He will be specially grateful for the excellent index.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



SPECTRA OF THE SODIUM ARC IN VACUO.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Zr.
Zirconium Pitchblende)
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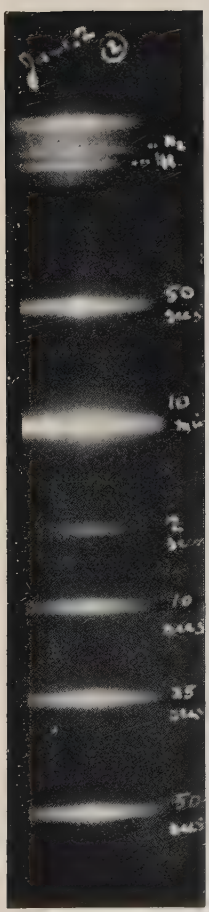
Scandium.
Short Exp.
Long Exp
Sc.
Carbon Arc.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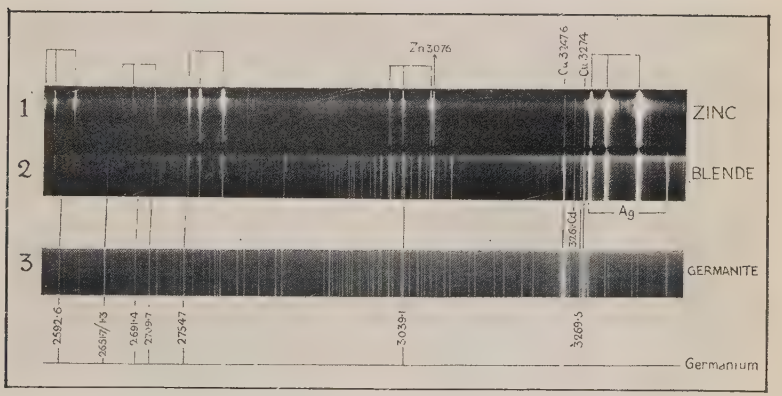
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3039·1
3269·5
Germanium

Fig. 3.

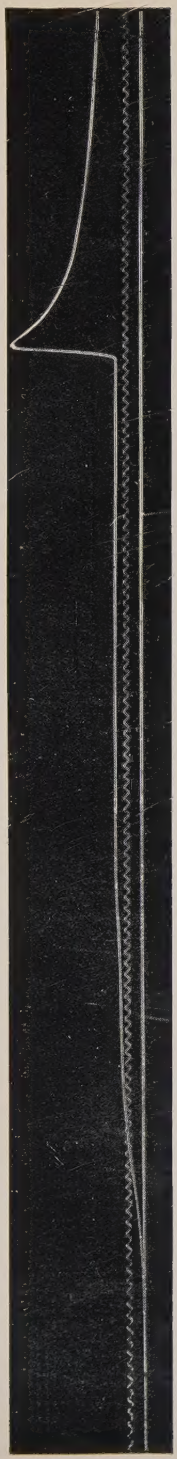
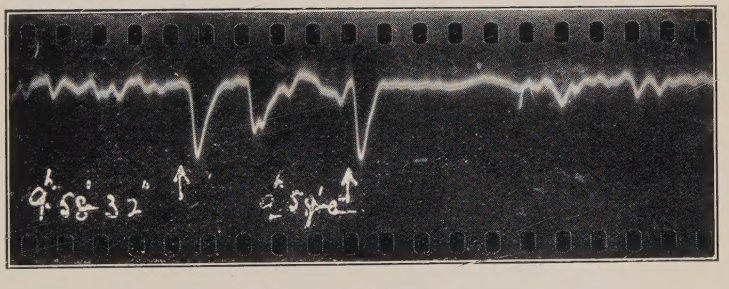
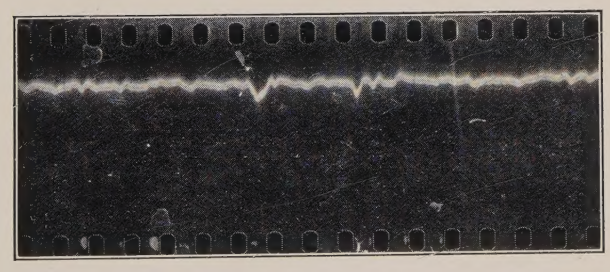


Fig. 4.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